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(54) **Discontinuous fiber and particulate reinforced refractory metal composite.**

(57) A method of making a reinforced refractory metal composite. A composition is prepared which comprises about 50 to about 99.9% by volume of niobium and about 0.1 to about 50% by volume of a particulate or fibrous dispersoid. The particulate dispersoid is an oxide, carbide, or boride of titanium, hafnium, zirconium, silicon, or a mixture thereof. The fibrous dispersoid is a carbide or boride of titanium, hafnium, zirconium, silicon, or a mixture thereof. The composition is mechanically alloyed in vacuum or in an inert atmosphere if a particulate dispersed is used. It is then hot pressed at a temperature greater than at 1000°C and a pressure greater than 70 atmospheres, and is extruded to form a shape. A fiber reinforced refractory metal composite made by this method is also described.

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DISCONTINUOUS FIBER AND PARTICULATE REINFORCED REFRACTORY METAL COMPOSITE

The invention relates to niobium-based refractory metal composites that are reinforced with either particulates or discontinuous fibers.

Materials used in nuclear power systems in outer space must be able to withstand elevated temperatures in excess of 1600K for long periods of time, radiation, liquid metal coolants, high fluence neutron irradiations, a vacuum, and high stresses. In addition, the materials should be lightweight, strong, ductile, and capable of being fabricated into various shapes. Very few materials can meet these stringent requirements.

The main object of the invention is to make a composite material that has these properties.

We have discovered that niobium-based alloys containing dispersions of particulates or fibers have excellent properties which make them very suitable for use in nuclear power systems in outer space. These composites have a high melting point, a low density, excellent ductility, irradiation swelling resistance, coolant compatibility, high elevated temperature strength, stability, and a high modulus. We have further found that the properties of these composites, where particulates are used, can be enhanced through the use of mechanical alloying in their fabrication. Additional enhancement is also attained by surface modification of fibers, where fibers are used, to prevent the formation of intermetallic compounds at the interface of the niobium matrix and the fibers; these intermetallic compounds tend to embrittle the composite and can lead to the formation of cracks

The matrix material for both fiber and particulate reinforced composite is niobium. While niobium itself can be used, it is preferable to use alloys of niobium as they are stronger. An alloy may contain any amount of the alloying metal, but it is preferable to use an alloy that contains about 50 to about 90% by weight niobium and about 10 to about 50% by weight of the alloying metal. Preferred alloying metals are tungsten, hafnium, zirconium, and mixtures thereof, as these alloying metals form the strongest alloys with niobium. Additional alloying elements such as carbon, oxygen, and nitrogen may be added. The matrix material is used in the form of a powder which can be of almost any particle size.

In the particulate reinforced composite, the dispersoid can be an oxide, carbide, or boride of titanium, hafnium, zirconium, silicon, or a mixture thereof. Particulate dispersoids are preferably about 1 to about 250 microns in particle size.

In the first step of the process of this invention for preparing the refractory metal composite using a particulate dispersoid, the dispersoid and the

matrix material are mixed together. About 20 to about 80% by volume of the matrix material is mixed with about 80 to about 20% by volume of the dispersoid.

The next step of the process of this invention is the mechanical alloying of the composition. Mechanical alloying is accomplished by placing the composition in an attritor, which is a high-speed ball mill operated under vacuum or in an inert atmosphere. The balls used in the attritor can be made of an inert material or they can be made of the same material which comprises the matrix material. The attritor is typically operated at room temperature or slightly above room temperature for the time, which may vary from hours to several days, necessary to disperse the dispersoid in the matrix material and produce a flake-like composite particulate.

In the next step of the process of this invention, the composition is cold pressed. Cold pressing reduces the volume of the composition and forms a low density green compact of 50 to 70% of theoretical density so that a vacuum can be easily applied in the next step of the process without drawing particles into the vacuum system. While cold pressing is an optional step, it is preferably performed as it facilitates handling in the next step. Cold pressing is preferably performed at room temperature, although higher or lower temperatures could also be used. Sufficient pressure should be used to increase the density to greater than 60% of theoretical density. Normally, a pressure in excess of 340 atmospheres will be required. Cold pressing is preferably performed isostatically so that the resulting shape has a uniform density throughout.

In the next step of the process of this invention, the green compact is consolidated, preferably by hot isostatic pressing, to a density greater than 90% of theoretical density; consolidation can also be accomplished by sintering or hot pressing. The cold pressed shape is enclosed in a can which is then evacuated to a pressure of less than 1×10^{-4} torr. While the temperature of consolidation will depend on the composition of the particular composite, temperatures in excess of 1000°C and pressures in excess of 680 atmospheres will normally be required. After consolidation, the densified compact can be extruded through a die to form a required shape.

In the fiber-reinforced composite, short fibers of a high strength material are used to strengthen the composite. The fibers, preferably about 1 to about 600 microns in diameter, can be carbides, borides, oxides, or nitrides of such elements as titanium, hafnium, zirconium, silicon, or mixtures

thereof. The fibers preferably have a length to diameter ratio of at least 5.

In the first step of the process of this invention using fibers, the surface of the fiber is modified. Surface modification is optional, but it is preferable to surface modify the fiber in order to help prevent the formation of intermetallic compounds at the interface of fiber and the matrix metal. Examples of methods of surface modification include coating the fiber or ion implanting the fiber surface. The fiber can be coated, for example, with silicon carbide or silicides of niobium or molybdenum or niobium diboride. This can be accomplished by evaporation with an electron beam, reactive evaporation or glow discharge method. The fibers can also be ion implanted using ions of, for example, helium, argon, or nitrogen to render a thin surface layer of the fiber amorphous.

In the next step of the process of this invention, the fibers and powdered matrix material are processed together. About 50 to about 90% by volume of the matrix material is mixed with about 50 to about 10% by volume of the fibers.

The mixture is preferably cold pressed to reduce the volume of the composite and form a green compact shape so that a vacuum can be used in the next step of the process, with ease, and without drawing the powders into the vacuum system. While cold pressing is an optional step, it is preferably performed as it simplifies processing at room temperature, although higher or lower temperatures could also be used. Sufficient pressure should be used to increase the density to greater than 50% of the theoretical density. Normally, a pressure in excess of 340 atmospheres will be required. Cold pressing is preferably performed isostatically so that the resulting shape has a homogeneous density.

In the next step of the process of this invention, the green compact shape is consolidated to full density by one of the several processes. For example, hot isostatic pressing can be used for this purpose. While the temperature required for hot isostatic pressing will depend on the particular composite being processed, temperatures in excess of 1000°C and pressures in excess of 680 atmospheres will normally be required. After hot isostatic pressing, the consolidated compact is extruded through a die to form a shape having a longitudinally aligned micro-structure. The shape can then be cut and machined as required. Options other than hot isostatic pressing such as hot pressing and sintering may also be employed following the cold pressing stage.

The following examples further illustrate this invention.

250 gm of ZrC, having a particle size of 5 microns, is mixed with 1200 gm of powdered alloy

of 80% niobium, 20% tungsten. The mixture is placed in an attritor and is mechanically alloyed for 24 hours at room temperature to produce a flake-like particulate. The particulate is cold pressed at greater than 340 atmospheres at room temperature. The resulting rod-shaped slug is then hot isostatically pressed at a temperature of 1000°C for 4 hours at greater than 680 atmospheres, and is then extruded through a die to form a shape.

250 gm of ZrC fibers having a length of 500 microns and 25 micron diameter is surface modified with an ion beam of about 10^{15} - 10^{16} ions/cm². Then 250 gm of fibers (density about 6.7 g/cm³) are mixed with about 1200 gm of powdered alloy of 80% niobium and 20% tungsten (density ~10.7 g/cm³). The mixture is cold pressed at greater than 340 atmospheres at room temperature to produce a rod-shaped green compact. The compact is hot pressed under argon or helium at 1200°C and 1700 atmospheres for 1 hour. It is then extruded through a die to form cylinder, rod, or tube as desired.

Claims

1. A method of making a reinforced refractory metal composite characterized by the steps of:

(A) preparing a composition which comprises:

- (i) about 50 to about 90% by volume of a metal which comprises niobium; and
- (ii) about 10% to about 50% by volume of a discontinuous fiber dispersoid selected from a group consisting of carbides, oxides, borides, nitrides, and mixtures thereof, of titanium, hafnium, zirconium, silicon, and mixtures thereof;

(B) consolidating said composition at a temperature greater than 1000°C and a pressure greater than 340 atmospheres; and

(C) extruding said composition into a shape.

2. A method according to Claim 1 characterized in that said metal is an alloy of niobium containing about 50 to about 99.5% by weight niobium.

3. A method according to Claim 1 characterized by the additional step of surface modifying said fibrous dispersoid before it is consolidated.

4. A method according to Claim 1 characterized by the additional step of cold pressing said composition to form a shape prior to said consolidating.

5. A method according to Claim 4 characterized in that said cold pressing is isostatic cold pressing at room temperature and a pressure greater than 340 atmospheres.

6. A method according to Claim 1 characterized in that said consolidating is by hot pressing.

7. A method according to Claim 6 characterized in that said hot pressing is hot isostatic pressing.

8. A method according to Claim 1 characterized in that said consolidating is by sintering.

9. A method according to Claim 1 characterized by the additional last steps of cutting and machining said extruded shape.

10. A method according to Claim 1 characterized in that said fibrous dispersoid has a diameter of about 1 to about 600 microns.

11. A composition characterized in that it includes:

(A) about 50 to about 90.5% by volume of a metal which comprises niobium; and

(B) about 10 to about 50% by volume of a fibrous dispersoid selected from the group consisting of titanium carbide, titanium boride, hafnium carbide, hafnium boride, zirconium carbide, zirconium boride, silicon carbide, silicon boride, and mixtures thereof.

12. A composition according to Claim 11 characterized in that said metal is an alloy of niobium.

13. A composition according to Claim 12 characterized in that said alloy is an alloy with a metal selected from the group consisting of tungsten, hafnium, zirconium, carbon, oxygen, nitrogen and mixtures thereof.

14. A composition according to Claim 11 characterized in that said fibrous dispersoid has a diameter of about 1 to about 600 microns.

15. A composition according to Claim 11 characterized in that said composition is hot pressed at a temperature greater than 1000°C and a pressure greater than 340 atmospheres and extruded.

16. A composite according to Claim 15 characterized in that said composition is cold pressed to form a shape at a pressure greater than 340 atmospheres prior to said hot pressing.

17. A composite according to Claim 15 characterized in that said fibrous dispersoid is surface modified.

18. A method of making a reinforced refractory metal composite characterized by the steps of:

(A) preparing a composition which comprises:

(i) about 50 to about 90% by volume of a metal which comprises niobium; and

(ii) about 10 to about 50% by volume of particulate dispersoid selected from the group consisting of oxides, carbides, borides, and mixtures thereof, of titanium, hafnium, zirconium, silicon, and mixtures thereof;

(B) mechanically alloying said composition in vacuum or inert atmosphere;

(C) consolidating said composition at a temperature greater than 1000°C and a pressure greater than 340 atmospheres; and

(D) extruding said composition into a shape.

19. A method according to Claim 18 characterized in that said metal is an alloy of niobium containing about 50 to about 99.5% by weight niobium.

20. A method according to Claim 18 characterized by the additional step of cold pressing said composition to form a shape after said mechanical alloying and prior to said consolidating.

21. A method according to Claim 20 characterized in that said cold pressing is isostatic cold pressing at room temperature and a pressure greater than about 340 atmospheres.

22. A method according to Claim 18 characterized in that said consolidating is by isostatic hot pressing.

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