Composite materials comprising a hard ceramic phase and an infiltration alloy are disclosed. The hard ceramic phase may comprise a carbide such as tungsten carbide and/or cast carbide. The infiltration alloy is a heat treatable Cu-based alloy comprising Ni and Mn. The infiltration alloy may be substantially free of Sn and Zn. The composite material is heat treated in order to improve its mechanical properties. For example, the composition of the Cu—Ni—Mn infiltration alloy may be selected such that its hardness, wear resistance, toughness and/or transverse rupture strength are improved after the composite material is solutionized, cooled and thermally aged.
Hard Ceramic Powder → Consolidate → Solutionize → Cool → Thermal Age

Cu-Ni-Mn Infiltration Alloy Powder
COMPOSITE MATERIALS COMPRISING A HARD CERAMIC PHASE AND A CU-NI-MN INFILTRATION ALLOY

FIELD OF THE INVENTION

[0001] The present invention relates to composite materials comprising a hard ceramic phase infiltrated with a metal alloy, and more particularly relates to the use of a Cu—Ni—Mn infiltration alloy which is susceptible to heat treatment and demonstrates improved properties.

BACKGROUND INFORMATION

[0002] Infiltration alloys are used with hard ceramics such as WC or cast carbides in drilling bit applications. To make such composite materials, a mold is filled with a mixture of ceramic powder and infiltration alloy powder, heated above the liquidus temperature of the infiltration alloy, and cooled to obtain a composite material. Examples of cutting tools comprising such composite materials are disclosed in U.S. Pat. Nos. 5,589,268, 5,733,649 and 5,733,664 which are incorporated herein by reference.

[0003] A conventional infiltration alloy comprises copper, manganese, nickel and tin. When such a Cu—Mn—Ni—Sn alloy is used in composite materials that are brazed to steel shanks of drill bits, a twist-off type of failure tends to occur at the interface between the composite material and the steel shank.

[0004] Another conventional infiltration alloy comprises copper, manganese, nickel and zinc. The use of such a Cu—Mn—Ni—Zn infiltration alloy may reduce or eliminate the above-mentioned twist off failure, but may also cause a drop in erosion resistance.

[0005] There is a need for a composite material comprising an infiltration alloy with improved erosion resistance and toughness.

SUMMARY OF THE INVENTION

[0006] The present invention provides composite materials comprising a hard ceramic phase and a Cu-based infiltration alloy. The hard ceramic phase may comprise carbides, borides, nitrides and oxides. Suitable carbides include tungsten carbide, tantalum carbide, niobium carbide, molybdenum carbide, chromium carbide, vanadium carbide, zirconium carbide, hafnium carbide, titanium carbide and cast carbides. Borides such as titanium diboride and other refractory metal borides may be used.

[0007] The Cu-based infiltration alloy is a heat treatable alloy which comprises Ni and Mn. In certain embodiments, the infiltration alloy is substantially free of Sn and Zn. The composite material may be heat treated in order to improve its mechanical properties. For example, the composition of the infiltration alloy may be selected such that its hardness, wear resistance, toughness and/or transverse rupture strength is improved after the composite material has been solutionized and aged at elevated temperatures. The composite materials are suitable for use in cutting tools and the like.

[0008] An aspect of the present invention is to provide a composite material comprising a hard ceramic phase, and a heat treated metal phase comprising a Cu-based infiltration alloy comprising Ni and Mn.

[0009] Another aspect of the present invention is to provide a method of making composite material comprising infiltrating an alloy into hard ceramic particles, wherein the infiltration alloy is a heat treatable alloy consisting essentially of Cu, Ni and Mn.

[0010] A further aspect of the present invention is to provide a method of heat treating a composite material comprising providing a composite material including a hard ceramic phase and an infiltration alloy comprising Cu, Ni and Mn, and heat treating the composite material.

[0011] These and other aspects of the present invention will be more apparent from the following description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIG. 1 is an isometric view of a cutting bit including a composite material of the present invention.

[0013] FIG. 2 schematically illustrates a fixture for consolidating composite materials with an embodiment of the present invention.

[0014] FIG. 3 is a flow diagram illustrating a method of forming and heat treating a composite material comprising a hard ceramic phase and a Cu—Ni—Mn infiltration alloy in accordance with an embodiment of the present invention.

DETAILED DESCRIPTION

[0015] A composite material comprising a hard ceramic phase and a Cu-based infiltration alloy is provided. The infiltration alloy is a Cu—Ni—Mn alloy that can be heat treated to improve the properties of the composite material. The heat treated Cu—Ni—Mn alloy may be substantially free of Sn and Zn. The composite material is useful for applications such as cutting tools.

[0016] FIG. 1 is an isometric view of a cutting bit 5 including a cutting head 6 made of a composite material of the present invention comprising a hard ceramic phase and a heat treated Cu—Ni—Mn infiltration alloy. Discrete diamond elements 7 may be bonded at the forward surface of the cutting head 6.

[0017] Suitable hard ceramic materials for use in accordance with the present invention include carbides, borides, nitrides and oxides. Suitable carbides for use as the hard ceramic phase include tungsten carbide, tantalum carbide, niobium carbide, molybdenum carbide, chromium carbide, vanadium carbide, zirconium carbide, hafnium carbide, titanium carbide and cast carbides. Suitable borides include titanium diboride and other refractory metal borides. Tungsten carbide may be particularly suitable as the hard ceramic phase, for example, in the form of sintered cemented macrocrystalline tungsten carbide particles.

[0018] In accordance with an embodiment of the present invention, the infiltration alloy is a heat treatable Cu—Ni—Mn alloy. As used herein, the term “heat treatable” means an alloy or composite containing the alloy which exhibit at least one improved mechanical property such as increased hardness, wear resistance, toughness and/or transverse rupture strength after the alloy or composite has been solutionized, cooled and thermally aged. During the solutionizing step, solute atoms are dissolved to form a single-phase solid solution. During the cooling step, the solutionized material is rapidly cooled or quenched, e.g., to room temperature, to form a supersaturated solid solution. During the thermal aging step, the supersaturated solid solution is heated to an intermediate temperature, i.e., within a two-phase region, at which second-phase precipitates form as finely dispersed particles. Lattice strains are established at the precipitate-matrix
interfaces, which provide increased resistance to dislocation motion. The heat treatable Cu—Ni—Mn infiltration alloy thus exhibits precipitation hardening as a result of the heat treatment process.

[0019] The amount of copper contained in the infiltration alloy typically ranges from about 30 to about 70 percent, for example, from about 55 to about 65 weight percent. As a particular example, the amount of copper may be about 60 weight percent.

[0020] The amount of Ni contained in the infiltration alloy typically ranges from about 15 to about 35 weight percent, for example, from about 18 to about 22 weight percent. As a particular example, the Ni content may be about 20 weight percent.

[0021] The amount of Mn contained in the infiltration alloy typically ranges from about 15 to about 35 weight percent, for example, from about 18 to about 22 weight percent. As a particular example, the Mn may comprise about 20 weight percent of the infiltration alloy.

[0022] The ratio of Ni to Mn may be controlled. For example, the atomic ratio of Ni:Mn may typically range from about 0.8:1 to about 1.2:1. In one embodiment, the atomic ratio of Ni:Mn may be 1:1. In another embodiment, the atomic ratio of Ni:Mn may be greater than 1:1, for example from about 1.0:1 to about 1.1:1 in order to increase the precipitation hardening effect.

[0023] In an embodiment of the present invention, the infiltration alloy is substantially free of Sn and Zn. As used herein, the term “substantially free of Sn and Zn” means that Sn and Zn are not purposefully added as alloying additions to the infiltration alloy, and are only present in the infiltration alloy up to trace amounts or as impurities.

[0024] The heat treated Cu—Ni—Mn infiltration alloy includes strengthening precipitates, e.g., in the form of an MnNi intermetallic material having a face centered tetragonal structure.

[0025] The relative amounts of the hard ceramic powder and Cu—Ni—Mn infiltration alloy powder may be selected in order to produce the desired ratio of ceramic phase and infiltration alloy phase in the final composite material. The hard ceramic phase is typically the most predominant phase of the composite material on a weight percentage basis. In one embodiment, the hard ceramic phase may comprise from about 60 to about 80 weight percent of the composite material, while the Cu—Ni—Mn infiltration alloy may comprise from about 20 to about 40 weight percent of the composite. As a particular example, the hard ceramic phase may comprise about 67 weight percent of the composite and the Cu—Ni—Mn infiltration alloy may comprise about 33 weight percent of the composite.

[0026] In addition to the above-noted hard ceramic and Cu—Ni—Mn infiltration alloy phases, the composite material may optionally include at least one additional phase. For example, the additional phase may comprise iron, 4000 steel, tungsten, cobalt, nickel, manganese, silicon, molybdenum, copper, zinc, chromium, boron, carbon, complex carbide eta phase materials, nitrides and/or carbonitrides. Eta phase materials are of the formula M₆C or M₃C₃ where M is a combination of carbide-forming metals such as Co, Fe, Ni and W, e.g., Co₃W₃C. Such optional additional phases may be present in the infiltration alloy in a total amount of up to about 5 weight percent.

[0027] FIG. 2 schematically illustrates a fixture for consolidating composite materials of the present invention. The production assembly shown in FIG. 2 includes a carbon mold, generally designated as 11, having a bottom wall 12 and an upstanding wall 13. The mold 11 defines a volume therein. The assembly further includes a top member 14, which fits over the opening of the mold 11. It should be understood that the use of the top number 14 is optional depending upon the degree of atmospheric control one desires.

[0028] A steel shank 17 is positioned within the mold before the powder is poured therein. A portion of the steel shank 17 is within the powder mixture 16 and another portion of the steel shank 17 is outside of the mixture 16. Shank 17 has threads 18 at one end thereof, and grooves 19 at the other end thereof.

[0029] Referring to the contents of the mold, a plurality of discrete diamonds 15 are positioned at selected positions within the mold so as to be at selected positions on the surface of the finished product. The ceramic matrix powder 16 is a carbide-based powder, which is poured into the mold 11 so as to be on top of the diamonds 15. Once the diamonds 15 have been set and the ceramic matrix powder 16 poured into the mold, a Cu—Ni—Mn infiltration alloy 20 of the present invention is positioned on top of the powder mixture 16 in the mold 11. Then the top 14 is positioned over the mold, and the mold is placed into a furnace and heated to approximately 1,200°C so that the infiltration alloy 20 melts and infiltrates the powder mass. The result is an end product wherein the infiltration alloy bonds the ceramic powder together, the matrix holds the diamonds therein, and the composite is bonded to the steel shank.

[0030] FIG. 3 schematically illustrates a method of forming and heat treating a composite material comprising a hard ceramic phase and a Cu—Ni—Mn infiltration alloy in accordance with an embodiment of the present invention. Hard ceramic powder is mixed with a Cu—Ni—Mn infiltration alloy powder and consolidated. Consolidation may be performed in a mold by heating the powder mixture above the liquidus temperature of the Cu—Ni—Mn infiltration alloy. During the consolidation step, temperatures of from about 1,100 to 1,200°C are typically used, for example, a consolidation temperature of about 1,200°C may be suitable. The consolidation temperature is held for a sufficient period of time to allow melting of the Cu—Ni—Mn infiltration alloy powder and bonding of the hard ceramic powder, such that a dense composite material is formed. The consolidation temperature may typically be held for a duration of from less than 1 minute to more than 5 hours. As a particular example, the consolidation temperature may be held for about 30 minutes.

[0031] The consolidated composite material may be cooled, e.g., to room temperature, followed by solutionizing at elevated temperatures, e.g., from about 500 to about 1,000°C, typically from about 750 to about 900°C. As a particular example, the solutionizing temperature may be about 850°C. Solutionizing at such elevated temperatures may typically be performed from 0.5 to 3 hours, for example, about 2 hours.

[0032] After the solutionizing step, the composite may be cooled to ambient temperature at a relatively fast cooling rate by any suitable means such as air cooling. The solutionized and cooled composite material may then be thermally aged at a temperature and time sufficient to increase at least one mechanical property of the composite. For example, aging temperatures may range from about 100 to about 450°C, typically from about 300 to about 450°C. As a particular example, a thermal aging temperature of about 430°C may be used. Typical thermal aging times may be from 0.5 to 72
Infiltration alloys listed in Table 1 were prepared. Alloy A is a Cu—Ni—Mn infiltration alloy in accordance with an embodiment of the present invention. Alloy B is a Cu—Mn—Ni—Zn alloy provided for comparison purposes.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Description</th>
<th>Content (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Cu—Ni—Mn Alloy</td>
<td>Cu 60, Ni 20, Mn 20, Sn 0, Zn 0</td>
</tr>
<tr>
<td>B</td>
<td>Cu—Mn—Ni—Zn Alloy</td>
<td>Cu 53, Mn 15, Ni 24, Zn 8</td>
</tr>
</tbody>
</table>

Table 1

Alloys in Table 1 were made in the form of roughly ¼ inch shots (Alloy A) or ½ inch cubes (Alloy B). Graphite molds were used to make infiltrated test specimens containing either an alloy or a mixture of 33% alloy and 67% P90 WC matrix powder comprising 67% macromorphine WC (~80 µm) and 31% of cast carbide (~325 mesh). The test specimens were made by heating the filled molds to 1,200°C under argon or hydrogen, holding at the temperature for 30 minutes, and cooling to room temperature. The specimens were determined to be impact toughness, B611 wear number, and transverse rupture strength (TRS). In the case of the Cu—Ni—Mn Alloy A, the following heat treatment was used on a number of specimens to assess the effectiveness of this treatment in improving the alloy properties: solutionize at 850°C; hold for 2 hours; air cool; age at 430°C for 8 to 72 hours; and air cool. Results of the tests are listed in Table 2.

Table 2

Properties of Tungsten Carbide and Infiltration Alloy Composites

<table>
<thead>
<tr>
<th>Alloy (As Cast)</th>
<th>A (Heat Treated)</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness (HV)</td>
<td>120</td>
<td>410</td>
</tr>
<tr>
<td>Impact Toughness (B-h)</td>
<td>1.0</td>
<td>2.5</td>
</tr>
<tr>
<td>B611 wear Number</td>
<td>0.67</td>
<td>0.98</td>
</tr>
<tr>
<td>TRS (ksi)</td>
<td>98</td>
<td>110</td>
</tr>
</tbody>
</table>

As shown in Table 2, mechanical properties of the composites including Alloy A may be dramatically increased by heat treatment in comparison with the conventional composite infiltrated with Alloy B. In accordance with embodiments of the present invention, it is possible to heat treat a Cu—Ni—Mn infiltration alloy to surpass properties such as wear resistance and TRS of conventional Cu-based infiltration alloys. Drilling bits made with the present spinodal infiltration alloys can be readily heat treated to obtain optimum combinations of service properties.

Whereas particular embodiments of this invention have been described above for purposes of illustration, it will be evident to those skilled in the art that numerous variations of the details of the present invention may be made without departing from the invention as defined in the appended claims.

1. A composite material comprising:
   a. a ceramic phase; and
   b. a metal phase comprising a heat treated Cu-based infiltration alloy comprising Ni and Mn, wherein the ceramic phase comprises from about 60 to about 80 weight percent of the composite material, the infiltration alloy comprises from about 20 to about 40 weight percent of the composite material, and the heat treated Cu-based infiltration alloy is substantially free of Sn.

2. The composite material of claim 1, wherein the heat treated Cu-based infiltration alloy comprises from about 15 to about 35 weight percent Ni, from about 15 to about 35 weight percent Mn, and the balance Cu and incidental impurities.

3. The composite material of claim 1, wherein the heat treated Cu-based infiltration alloy comprises from about 18 to about 22 weight percent Ni, from about 18 to about 22 weight percent Mn, and the balance Cu and incidental impurities.

4. The composite material of claim 1, wherein the heat treated Cu-based infiltration alloy is substantially free of Sn.

5. (canceled)

8. The composite material of claim 1, wherein the ceramic phase comprises at least one carbide selected from tungsten carbide, titanium carbide, tantalum carbide, niobium carbide, molybdenum carbide, chromium carbide, vanadium carbide, zirconium carbide and hafnium carbide.

9. The composite material of claim 8, wherein the carbide comprises WC.

10. The composite material of claim 1, further comprising at least one additional phase.

11. The composite material of claim 10, wherein the at least one additional phase comprises iron, 4600 steel, tungsten, cobalt, nickel, manganese, silicon, molybdenum, copper, zinc, chromium, boron, carbon, nitrides and/or carbonitrides.

12. The composite material of claim 1, further comprising Co.

13. The composite material of claim 1, wherein the composite material has been subjected to thermal aging at a temperature of from about 100°C to about 450°C for a time of from about 0.5 to about 72 hours.

14. A method of making a composite material comprising infiltrating an alloy into ceramic particles, wherein the infiltration alloy consists essentially of Cu, Ni and Mn and is substantially free of Zn, the ceramic particles comprise from about 60 to about 80 weight percent of the composite material, and the infiltration alloy comprises from about 20 to about 40 weight percent of the composite material; and heat treating the composite material.

15. The method of claim 14, wherein the infiltration alloy comprises from about 15 to about 35 weight percent Ni, from about 15 to about 35 weight percent Mn, and the balance Cu and incidental impurities.

16. The method of claim 14, wherein the infiltration alloy comprises from about 18 to about 22 weight percent Ni, from about 18 to about 22 weight percent Mn, and the balance Cu and incidental impurities.

17. The method of claim 14, wherein the infiltration alloy is substantially free of Sn.

18. (canceled)

19. The method of claim 14, wherein the ceramic particles comprise WC.
20. (canceled)

21. The method of claim 14, wherein the heat treating includes thermal aging at a temperature of from about 100 to about 450°C for a time of from about 0.5 to about 72 hours.

22. A method of heat treating a composite material comprising:

- providing a composite material including a ceramic phase and an infiltration alloy comprising Cu, Ni and Mn, wherein the ceramic phase comprises from about 60 to about 80 weight percent of the composite material, the infiltration alloy comprises from about 20 to about 40 weight percent of the composite material, and the infiltration alloy is substantially free of Zn; and
- heat treating the composite.

23. The method of claim 22, wherein the heat treating includes thermal aging at a temperature of from about 100 to about 450°C for a time of from about 0.5 to about 72 hours.

24. The method of claim 23, wherein the heat treating comprises solutionizing the infiltration alloy at an elevated temperature and cooling the solutionized infiltration alloy prior to the step of thermally aging the composite.

25. The method of claim 24, wherein the solutionizing step is performed at a temperature of from about 500 to about 1,000°C for a time of from about 0.5 to about 3 hours.

26. The method of claim 24, wherein the solutionized infiltration alloy is cooled to room temperature prior to the step of thermally aging the composite.

27. The method of claim 22, wherein the heat treated Cu-based infiltration alloy comprises from about 15 to about 35 weight percent Ni, from about 15 to about 35 weight percent Mn, and the balance Cu and incidental impurities.

28. The method of claim 22, wherein the heat treated Cu-based infiltration alloy comprises from about 18 to about 22 weight percent Ni, from about 18 to about 22 weight percent Mn, and the balance Cu and incidental impurities.

29. The method of claim 28, wherein the infiltration alloy is substantially free of Sn.

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