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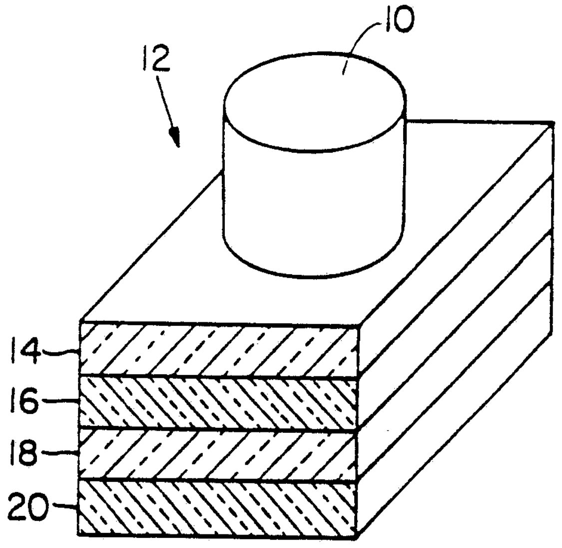

(57) Abstract

Prepare hardened cermets by: forming a porous ceramic compact that contains a first, or metal component reactive, ceramic component, and a second, or substantially nonreactive, ceramic component; at least partially filling the pores with a metal component to form a metal-filled ceramic compact; exposing the metal-filled compact to an elevated temperature to form a cermet-hardening component; and cooling the resultant compact to form a hardened cermet. Laminates of hardened cermets having differing ratios of first to second ceramic components can also be formed.

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HARDENED CERMETS AND METHOD OF FORMING HARDENED CERMETS

Cermets are refractories that include at least one ceramic component and at least one metal component. The mechanical properties of cermets often depend upon the relative amounts of ceramic and metal components present. For example, metal components, such as aluminum (Al), are less hard than ceramic components, such as aluminum nitride (AlN). Therefore, a cermet including a low proportion of aluminum to aluminum nitride will be harder than a cermet including a higher proportion of aluminum to aluminum nitride. The relative hardness of a cermet is, however, inversely proportional to its resistance to damage as a result of repeated impacts.

Cermets are typically formed by substantially filling the pores of a porous ceramic compact with a molten metal. Upon cooling, the molten metal solidifies thereby forming the cermet. The relative amounts of metal and ceramic components are generally limited by the ability of the metal to fill the pores of the porous ceramic compact. If the pores are too small, molten metal often will not substantially fill the pores. Alternatively, if the pores are too large, the amount of molten metal required to fill the pores can be excessive, thereby causing the resulting cermet to lack sufficient hardness.

One attempt to form cermets that exhibit both relatively high hardness and high impact resistance employs only extremely hard ceramic components, such as titanium diboride (TiB_2) or boron carbide (B_4C). However, such ceramic components have poor resistance to repeated impact, hereinafter "multi-impact resistance", as opposed to resistance to a single impact, hereinafter "single-impact resistance"

Another attempt disposes a molten metal in a porous ceramic that has a void space greater than the volume of molten metal. Exposure to a combination of temperature and pressure sufficient to at least partially densify the porous ceramic causes a substantial portion of the pores either to collapse or to fill with molten metal. Such exposure can, however, cause significant shrinkage and deformation of the ceramic component, thereby forming a defective cermet. Also, exposure to very high temperatures and pressures can result in a variety of reaction products. Brittle reaction products significantly diminish the impact resistance of the resulting cermet. Comparatively soft reaction products similarly diminish the hardness of the resulting cermet.

Thus, a need exists for cermets and a method of forming cermets which overcome or minimize the above-mentioned problems.

One aspect of the present invention is a process for forming a hardened cermet, comprising the steps of: a) providing a porous ceramic compact including a first ceramic component and a second ceramic component; b) at least partially filling pores of the porous ceramic compact with a molten metal component to form a metal-filled ceramic compact; c) exposing the metal-filled ceramic compact to a sufficient temperature for a sufficient time period to cause at least a portion of the first ceramic component to react with at least a portion of the molten metal component and form a cermet-hardening component, the second ceramic component undergoing no significant reaction with the molten metal at said temperature; and d) cooling the metal-filled ceramic compact and cermet-hardening component to a temperature that allows the remainder of the molten metal component to solidify, thereby forming a hardened cermet.

A second aspect of the present invention is a hardened cermet that comprises: a) providing a layered assembly having a first porous ceramic layer and at least one additional porous ceramic layer, the first and additional layers including a first ceramic component and a second ceramic component, each layer within said layered assembly having a ratio of the first ceramic component to the second ceramic component that differs from the ratio within each adjacent layer; b) at least partially filling pores within each layer with a molten metal component to form a metal-filled layered assembly; c) exposing the assembly to a sufficient temperature for a time period sufficient to cause at least a portion of the first ceramic component in each layer to react with at least a portion of the metal component contained therein to form a cermet-hardening component, the second ceramic component undergoing no significant reaction with the molten metal at said temperature; and d) cooling the assembly resulting from step (c) to a temperature that allows any remaining molten metal to solidify, thereby forming a hardened cermet laminate.

This invention has many advantages. Hardened cermets can be formed that are relatively hard, as a consequence of forming the cermet-hardening component, and have relatively high multi-impact resistance, because of residual metal component. The amount of relatively hard, expensive ceramic components needed to form correspondingly hard cermets can also be significantly reduced. In addition, the hardness and impact resistance of the resulting cermet can be controlled by limiting the extent of reaction between molten metal and a reactive ceramic component in a metal-filled ceramic. Further, hardened-cermet laminates that have distinct layers of varying physical properties or thicknesses can be formed.

Figure 1 is a perspective view of a porous ceramic assembly on which an amount of metal powder is disposed prior to infiltration to form a metal-filled ceramic assembly.

Figure 2 is a perspective view of the metal-filled ceramic assembly prior to formation of a cermet-hardening component.

Figure 3 is a hardened cermet laminate formed from the metal-filled ceramic assembly illustrated in Figure 2 and having layers of progressively differing hardness and impact resistance.

The features and other details of the present invention are more particularly described with reference to the accompanying drawings and pointed out in the claims. The same number present in different figures represents the same item. The particular embodiments of the invention shown in the drawings illustrate, but do not limit, the invention. The principle features of this invention can be employed in various embodiments without departing from its scope.

Hardened cermets of the present invention are formed from a metal component and a porous ceramic compact that includes at least two ceramic components. The metal is suitable for reaction with at least one of the ceramic components to form a cermet-hardening component. Examples of suitable metals include cobalt, chromium, iron, hafnium, manganese, molybdenum, niobium, nickel, scandium, silicon, tantalum, technetium, thorium, vanadium, tungsten, yttrium, zirconium, magnesium, aluminum and alloys or mixtures of two or more of such metals. The metal is preferably aluminum, silicon, magnesium, titanium or an alloy or mixture of two or more of such metals.

At least one of the ceramic components, designated a first ceramic component, must react with at least a portion of the metal component to form the cermet hardening component. The reaction occurs at a temperature greater than or equal to one-half of the metal component's melting point, but less than the lowest decomposition or melting temperature of the ceramic components. The reaction proceeds much faster at or above a metal component's melting temperature that at one-half said temperature. At least one of the ceramic components, designated a second, or relatively nonreactive, ceramic component, yields little, if any, reaction product at such a temperature. The temperature is maintained for a period of time sufficient to produce a desired amount of the cermet hardening component. By way of illustration, when the metal component is aluminum, the first ceramic component is boron carbide and the second ceramic component is titanium diboride, the period of time ranges from one hour to 100 hours. The period of time preferably ranges from 20 to 50, most preferably 25 to 40, hours at a temperature within a range of 600 to 2350°C. The respective melting points for aluminum, boron carbide and titanium diboride are 660.37°C, 2350°C and 2900°C. Although the reaction starts at about 450°C, significant amounts of new phases do not appear at temperatures below 600°C. The range is preferably 600 to 1000°C. When the metal component is aluminum and the first ceramic component is boron carbide, the second ceramic component may be boron carbide that is heat treated to reduce its reactivity with aluminum. The boron carbide heat treatment occurs at a temperature in excess of 1600°C, preferably above 1800°C, but less than 2350°C. Heat treatment times of from 30 minutes to 5 hours produce satisfactory results. Exposure times for metal-filled ceramic compacts of 1 to 50 hours, preferably 20 to 30 hours, and temperatures within a range of 600 to 1000°C produce satisfactory results.

When the metal component is aluminum, the first and second components may both be boron carbide if one condition is met. That condition is that the first component must be fine, or less than 5 micrometers average particle diameter, and the second component must be large, or greater than 45 micrometers average particle diameter. Reaction times of 2-20 hours at temperatures within a range of 600 to 1000°C produce satisfactory results.

Examples of suitable combinations of metal components and first ceramic components include: boron carbide (B_4C) and magnesium (Mg) (m.pt. 648.8°C); boron carbide and titanium (Ti) (m.Pt. 1660 ± 10°C); aluminum boride (AlB_{12}) and iron (Fe) (m.pt. 1535°C); boron carbide and manganese (Mn) (m.pt. 1244 ± 3°C) and boron carbide and zirconium (m.pt 1852 ± 2°C). Examples of combinations of metals and second ceramic components include: aluminum (Al) and aluminum nitride (AlN) (sublimes at 2000°C); aluminum and aluminum oxide (Al_2O_3) (m.pt. 2072°C); titanium and titanium carbide (TiC) (m.pt. 3140 ± 90°C); titanium and titanium diboride (TiB_2) (m.pt. 2900°C); and magnesium and magnesium oxide (MgO) (m.pt. 2852°C). Preferably, the metal component includes aluminum, the first ceramic component includes boron carbide (B_4C) and the second ceramic component includes titanium diboride (TiB_2).

In one embodiment of the invention, a porous ceramic compact is formed by a conventional method. For example, the first ceramic component and the second ceramic component are combined as a powder mixture. The powder mixture is then mixed with water, a suitable binder, and a dispersant or lubricant, or both, to form a wet mixture. The wet mixture is formed into a suitable porous ceramic compact by a conventional method, such as slip casting, centrifugal casting or injection molding. The porous ceramic compact can be in the form of ceramic greenware. The porous compact can also be partially densified by a suitable method, such as sintering, hot pressing or hot isostatic pressing. The porous ceramic compact can have many different shapes, including cylinders, discs, cones, spheres, cubes. The shape can also approximate that of the hardened cermet to be formed.

Conventional methods suitably result in pores of the porous ceramic compact being substantially filled with the metal component. The volume of the pores is preferably in a range of from five to fifty percent by volume, based upon total volume of the porous ceramic. In a particularly preferred embodiment, an average pore diameter is between 0.5 and five micrometers.

The relative amounts of first and second ceramic components affect the amount of cermet-hardening component formed in accordance with the present invention. When the metal is aluminum and its first and second ceramic components are, respectively, boron carbide and titanium diboride, a desirable volumetric ratio of boron carbide to titanium diboride is within a range of between 90:10 and 10:90. The range is preferably between 90:10 and 60:40, most preferably between 80:20 and 70:30.

The amount of metal component is preferably sufficient to at least partially fill the pores of the porous ceramic compact and react with the first ceramic component to form an amount of cermet-hardening component sufficient to significantly harden the resulting cermet. The term "significantly harden" means an increase in hardness, in comparison to the same cermet without a hardening component, of at least 15%, preferably at least 25%. Preferably, the amount is within a range of between five and fifty percent of the volume of the porous ceramic compact. A more preferred range for partially filled compacts is from 5 to 10 volume percent. A more preferred range for preparing compacts that are near theoretical density is from 20 to 50 volume percent.

Conventional means are used to at least partially fill pores of the porous ceramic compact with molten metal component to form a metal-filled ceramic. For example, the metal component is combined, as a metal powder, with the ceramic powder mixture during formation of the porous ceramic compact or porous greenware. The greenware is then exposed to sufficient temperature and pressure for a sufficient time period to cause the metal component to become molten and at least partially fill the pores of the porous ceramic greenware. An example of a suitable method of exposing the porous ceramic greenware to pressure is rapid omnidirectional compaction. When aluminum is the metal component and boron carbide and titanium diboride are, respectively, the first and second ceramic components, desirable rapid omnidirectional compaction conditions include a temperature within a range of from 660°C to 1,200°C, a pressure within a range of from 1 MPa to 850 MPa, and a time at pressure within a range of from five seconds to one hour. The temperature range is preferably 700 to 1000°C, most preferably 700 to 900°C. The pressure range is preferably 180 to 850 MPa, most preferably 800 to 830 MPa. The time is preferably 30 seconds to ten minutes, most preferably 30 to 90 seconds.

Alternatively, molten metal can substantially fill the pores of the porous ceramic compact by vacuum or pressure infiltration. The porous ceramic compact is preferably exposed to a temperature within a range of from 1,600°C to 2,250°C for a period of time within a range of from thirty to sixty minutes before infiltration. The metal component is placed in contact with the porous compact, desirably on its top or bottom surface. The metal component and the porous compact are then exposed to conditions of temperature and pressure sufficient to melt the metal component and cause it to flow into, and at least partially fill, the pores of the porous compact. Gravitational force, capillary attraction, or applied pressure can assist infiltration.

In a preferred embodiment, including aluminum, boron carbide and titanium diboride, the porous ceramic compact and the aluminum are heated to an infiltration temperature within a range of from 1,100°C to 1,200°C. During infiltration, the porous ceramic compact and the molten aluminum are subjected to a reduced pressure or vacuum within a range of from 10 to 300 millitorrs (1.3 to 44 pascals). In some embodiments, the atmosphere includes an inert gas such as argon.

The metal-filled of infiltrated ceramic is then exposed to a sufficient temperature for a sufficient time period to cause at least a portion of the first ceramic component to react with at least a portion of the molten metal component to form the cermet-hardening component. The temperature is desirably within a range of from 600°C to 1500°C, preferably from 700 to 1200°C. The time period is desirably within a range of from 0.5 to 50 hours, preferably 30 to 50 hours. The metal-filled ceramic can, however, be cooled to a temperature that allows the metal to solidify and thereby form a cermet before exposing the cermet to conditions sufficient to form the cermet-hardening component.

Although the mechanism of the invention is not completely understood, it is believed that the cermet-hardening component is significantly harder than the unreacted combination of the metal component and the first ceramic component. It is also believed that the presence of the second ceramic component interferes with, and slows the rate of, reaction between the metal and first ceramic component. An added degree of control over the reaction is thus provided by the presence of the second ceramic component.

When the metal-filled ceramic is an aluminum-filled ceramic that includes boron carbide and titanium diboride, it is heat-treated by exposure to a temperature within a range of from 600°C to 1,000°C for a period of time within a range of from one to fifty hours. Heat treatment preferably occurs in an inert gas atmosphere at a pressure within a range of from one to ten atmospheres (0.10 to 1.01 MPa). The heat treatment conditions are sufficient to cause a reaction between boron carbide and molten aluminum.

Boron carbide and molten aluminum react at temperatures within a range of from 600°C to 1,000°C to form AlB_2 and Al_4BC. Solidification of the AlB_2 and Al_4BC causes the resulting cermet to be significantly harder than a cermet including only aluminum and boron carbide or only aluminum and titanium diboride. By way of illustration, cermets that contain 30 volume % aluminum and 70 volume % of either boron carbide or titanium diboride but no hardening component have a hardness within a range of 200 to 450 kg/mm^2. After heat treatment to form the hardening component, the hardness increases to a value within a range of 800 to 1400 kg/mm^2. Al_4BC, while significantly harder than AlB_2, can decompose to form AlB_2, a more stable compound. It is believed that the presence of the second ceramic component in the porous ceramic compact slows both the reaction between the aluminum and B_4C to form AlB_2 and Al_4BC and the decomposition of Al_4BC to AlB_2.

The metal-filled ceramic and the cermet hardening component contained therein are then cooled to a temperature that stops the reaction and allows any remaining molten metal to solidify. The presence of the cermet-hardening component converts the cermet to a hardened cermet.

The amount of remaining molten metal is preferably sufficient to prevent the hardened cermet's multi-impact resistance from being significantly less than that of a cermet formed without any significant reaction between the molten metal component and the first ceramic component. In a particularly preferred embodiment, the amount of metal component in the hardened cermet is within a range of from 3 to 30% by weight of the hardened cermet. A still more preferred range is 5 to 15% by weight.

Hardened cermets formed by the method of the invention can be employed to form hardened-cermet laminates. The hardened-cermet laminates can include cermet layers having various ceramic components and varying amounts of common ceramic components.

In one illustration, a hardened-cermet laminate is formed by disposing aluminum disc 10 on porous ceramic assembly 12, as shown in Figure 1. The volume of disc 10 is sufficient to at least partially fill the pores of assembly 12. Assembly 12 includes vertically stacked, partially densified, porous ceramic layers 14,16,18 and 20. The amount of void space in each porous ceramic layer is preferably within a range of from fifteen to forty percent of the total volume of the porous ceramic layer. Layers 14,16,18 and 20 are bonded together by densifying the layers as a stacked assembly of greenware layers. Layers 14,16,18 and 20 can, however, be ceramic greenware rather than partially densified. The greenware layers are bonded together during formation of the hardened-cermet laminate.

Boron carbide is present, as a first ceramic component, in porous ceramic layers 14,16,18 and 20 in the respective amounts of seventy, eighty, ninety and one hundred percent, by volume, of the total volume of the ceramic components. The balance of the ceramic in each porous ceramic layer is titanium diboride, as a second ceramic component.

Aluminum disc 10 and porous ceramic assembly 12 are disposed in a suitable furnace, such as a graphite vacuum furnace, and exposed to an atmosphere and temperature sufficient to cause aluminum disc 10 to melt, infiltrate and at least partially fill the pores of porous ceramic assembly 12. Preferably, a vacuum is present in the furnace at a reduced pressure within a range of from ten to three hundred millitorrs (1.3 to 40 Pascals). Also, the temperature is preferably maintained within a range of from 1,150 to 1,200°C for a time of from 30 minutes to 2 hours during infiltration.

Infiltration of porous ceramic assembly 12 by molten aluminum causes formation of metal-filled ceramic assembly 22, including metal-filled ceramic layers 24,26,28 and 30, as shown in Figure 2. Assembly 22 is then exposed to a sufficient temperature for a sufficient time period to cause at least a portion of the boron carbide in layers 24,26,28 and 30 to react with at least a portion of the molten aluminum and form a cermet-hardening component. In this embodiment, the cermet-hardening component includes a combination of Al_4BC and AlB_2. Satisfactory results are obtained with a temperature within a range of 700 to 900°C and a time within a range of 30 to 50 hours.

The amount of Al_4BC present in each of metal-filled ceramic layers 24,26,28 and 30, relative to the amount of AlB_2, depends, at least in part, upon the relative amount of second ceramic component, in this case titanium diboride, present in each layer. For example, the proportion of Al_4BC to AlB_2 is highest in layer 24. Layer 24 has the greatest amount of titanium diboride relative to layers 26,28 and 30. Similarly, layer 26 includes a greater ratio of Al_4BC to AlB_2 than layers 28 and 30, and layer 28 includes a greater ratio of Al_4BC to AlB_2 than layer 30. Thus, a discreet gradation of the ratio of Al_4BC to AlB_2 is distributed in assembly 22 from layer 24 to layer 30.

Assembly 22 and the cermet-hardening component contained therein are then cooled to a temperature that allows the remainder of the molten aluminum to solidify, thereby forming hardened-cermet laminate 32 shown in Figure 3. A suitable cooling rate is 2 to 5°C per minute to room temperature. Laminate 32 includes hardened-cermet layers 34,36,38 and 40. Layers 34,36,38 and 40 are bonded together by aluminum that has solidified between the cermet layers.

The amount of cermet-hardening component formed, relative to the amount of the combined first and second ceramic components present, is highest in layer 40. Conversely, the relative amount of cermet-hardening component is lowest in layer 34. However, because the decomposition of Al_4BC to AlB_2 is significantly diminished in layer 34, by comparison to layer 40, and because Al_4BC is significantly harder than AlB_2, layer 34 has substantially the same hardness as layer 40. Similarly, layer 36 and layer 38 have substantially the same hardness as layer 40.

The amount of the second ceramic component, titanium diboride, diminishes in amount from layer 34 to layer 40. It appears that the reaction of aluminum and B_4C to form the cermet-hardening component varies in direct relation to the relative amount of the second ceramic component present in a layer. Therefore, the amount of unreacted metal component, aluminum, relative to the combined amount of unreacted first and second components present, is highest in layer 34 and diminishes from layer 34 to layer 40. The multi-impact resistance of each layer is directly proportional to the relative amount of metal component present in each layer. Consequently, layer 34 has the greatest multi-impact resistance of the layers in laminate 32. Also, laminate 32 exhibits a gradient of increasing multi-impact resistance from layer 40 to layer 34, as indicated by arrow 42.

Conversely, the single-impact resistance is directly proportional to the ratio of the combined amount of the unreacted ceramic components to the unreacted metal component. Therefore, the single-impact resistance of laminate 32 is greatest at layer 40. Also, laminate 32 exhibits a gradient of increasing impact resistance from layer 34 to layer 40, as indicated by arrow 44.

Alternative, hardened cermet laminates that include arrangements of hardened-cermet layers other than that described in Figures 1 through 3 can be formed. For example, the hardened cermet layers can alternate between relatively hard and relatively impact resistant hardened cermets. Also, the relative thickness of the hardened cermet layers can vary.

The invention will now be further and more specifically described by the following examples. All parts and percentages are by weight unless otherwise stated.

Example I

Seven pairs of porous ceramic greenware discs were formed from compositions that included boron carbide (B_4C) and titanium diboride (TiB_2) as ceramic components. Each pair of greenware discs included different relative amounts of the two ceramic components. The volumetric ratio of boron carbide to titanium diboride in the seven pairs of greenware discs were as follows: 1:0; 9:1; 7:3; 1:1; 3:7; 1:9; and 0:1. The discs had a diameter of three inches (7.6 cm) and a thickness of 0.5 inches (1.3 cm). The discs had an average theoretical density within a range of from 62 to 64 percent.

The disks were each placed in a refractory crucible formed of graphite so that a flat upper side of the disk was substantially level. The refractory crucibles, within which the discs were disposed, were placed in a graphite-element furnace. Two hundred grams of 1145 grade aluminum powder, commercially available from Alcoa, Inc., were disposed on the level surface of each disc.

The furnace was then sealed and vacuum-purged three times and then filled with an argon gas that included five percent hydrogen by volume. The pressure of the furnace was then reduced to 150 millitorrs (20 Pa) and the temperature in the furnace was raised at a rate of 20°C per minute to a temperature of 1180°C. The temperature in the furnace was maintained at 1180°C for one-half hour to allow the aluminum to substantially infiltrate the pores of the discs, thereby forming metal-filled ceramic discs. The metal-filled ceramic discs were subsequently allowed to cool at a rate of about 10°C per minute to a temperature of 100°C. The aluminum in the metal-filled aluminum discs solidified to cause the metal-filled discs to form cermet discs. One cermet disk of each pair was then removed from the furnace and labeled as a control disc.

The furnace was filled with argon gas, the pressure was increased to one atmosphere (1.01×10^5 Pa) and the temperature of the furnace, including the cermet discs remaining in the furnace, was raised at a rate of 20°C per minute to a temperature of 900°C. The temperature in the furnace was maintained at 900°C for twenty hours to form a cermet-hardening component. The cermet disks were subsequently allowed to cool at a rate of 10°C per minute to a temperature of 20°C to thereby form hardened cermet discs.

The control disks and the hardened cermet discs were tested for hardness. The hardness test was a Vicker's hardness test, using a thirty pound (13.6 Kg) load. The results of hardness testing are listed below in Table I:

As can be seen in Table I, the hardness of the control disks, with no post-infiltration heat treatment, diminished significantly as the ratio of boron carbide to titanium diboride

Table I

Ceramic Content (by volume)		Hardness (Kg/mm2)	
Boron carbide	Titanium diboride	Control	Hardened
100	0	895	1384
90	10	790	1415
70	30	640	1375
50	50	568	1072
30	70	503	766
10	90	358	413
0	100	214	229

present in the disks decreased from 100:0 to 70:30. In contrast, there was no significant loss of hardness over the same decrease of relative boron carbide content in the hardened cermets. Also, as the ratio of boron carbide to titanium diboride decreased to 70:30, the difference in hardness between the control disks and the corresponding hardened cermet disks increased. Therefore, as the proportion of titanium diboride increased up to about thirty percent of the greenware ceramic discs, by volume, the percentage increase of hardness achieved was improved by exposing the cermet disks to a post-infiltration heat-treatment according to the method of the invention.

Example II

Four sets of porous ceramic greenware discs were formed with boron carbide (B_4C) and titanium diboride (TiB_2) as ceramic components. Each set of greenware discs included five discs having the same proportion of boron carbide to titanium diboride. The ratio of boron carbide to titanium diboride of the four sets of greenware discs were as follows: 1:0; 9:1; 8:2; and 7:3. The greenware discs had the same dimensions and theoretical density as the greenware discs of Example I.

The disks were disposed in a refractory crucible that was placed in the furnace described in Example I. The furnace was vacuum-purged three times, as described in Example I, and then filled with argon gas under atmospheric pressure. The temperature in the furnace was raised at a rate of 20°C per minute to a temperature of 2250°C and maintained at that temperature for about forty minutes to partially densify the greenware discs The temperature in the furnace was then lowered at rate of about 20°C per minute to a temperature of 20°C. The resulting partially densified greenware disks had a theoretical density within a range of from seventy-five to seventy-seven percent.

About 200 gms of 1145 grade aluminum powder, commercially available from Alcoa, Inc., were disposed on a flat surface of each partially densified disk. The furnace was purged three times, as in Example I, and the pressure within the furnace was set at about 125 millitorr (16.7 Pa). The temperature in the furnace was then raised, as in Example I, to 1180°C and maintained at that temperature for one-half hour to allow the aluminum to infiltrate and substantially fill the partially densified discs, thereby forming metal-filled discs. The furnace was then cooled, at as in Example I, to a temperature of 20°C.

One metal-filled disk of each set was then immediately removed from the furnace and labeled as a control disc. The remaining disks were exposed to a heat-treatment temperature of 900°C in the furnace to allow a cermet-hardening component to form. A metal-filled disk of each set was subsequently removed from the furnace after eight, fifteen, twenty and fifty hours of exposure to the heat-treatment temperature of 900°C in the furnace. Metal-filled discs removed from the furnace were cooled at a rate of about 20°C per minute to form hardened cermets.

The hardness of all resulting discs was determined by the Vicker's hardness test, as described in Example I. The test results are shown below in Table II:

Table II

Ceramic Content (by volume)			Hardness (Kg/mm^2)				
Boron Carbide	Titanium Diboride	Time (hrs)	Ctrl	8	15*	20	50
100	0		807	822	-	787	814
90	10		914	920	-	1431	1431
80	20		897	931	940	1381	1529
70	30		950	1075	1485	1489	1599

* - means not measured

As can be seen in Table II, all of the partially densified discs that included titanium diboride were hardened by exposure to heat-treatment following infiltration. In contrast, the partially densified control discs, which did not include titanium diboride, were not significantly hardened under the same conditions. Therefore, the presence of titanium diboride allowed a significant increase in hardness of the resulting cermets.

Example III

A set of six porous ceramic greenware discs was formed that included only boron carbide as a ceramic component. Another set of six porous ceramic greenware discs was formed that included sixty percent boron carbide and forty percent of titanium diboride, both percentages based on volume of ceramic. The greenware discs had the same dimensions and range of theoretical densities as the greenware disks described in Examples I and II.

The greenware disks were disposed in a furnace and infiltrated with aluminum to form metal-filled ceramic discs, as described in Example I. The temperature of the furnace was then lowered from 1180°C to 925°C. One metal-filled disc from each set was then removed from the furnace and labeled as a control disc. The remaining metal-filled ceramic discs were maintained at a temperature of 925°C in the furnace to form a cermet-hardening component. An additional metal-filled disc was removed at five, eight, fifteen, twenty and fifty hours after lowering the furnace temperature to 925°C. The temperature of discs removed from the furnace was lowered, as described in Example I, to allow the remaining, unreacted aluminum to solidify, thereby forming cermet discs.

The hardness of the cermet discs was determined using the Vicker's hardness test, as described in Example I. The test results are shown below in Table III:

Table III

Ceramic Content (% vol)			Hardness (Kg/mm^2)					
B_4C	TiB_2	Time (hr)	0	5	8	15	20	50
100	0		1175	1334	1387	1384	1386	1260
60	40		848	959	1148	1280	1304	1384

As can be seen in Table III, the hardness of the cermet disc, that included only boron carbide as the ceramic component and that was exposed to post-infiltration heat treatment for fifty hours, was less hard than other cermet discs of the same set that were exposed to the same heat treatment for between about five and twenty hours. In contrast, the cermet disc, that included titanium diboride as a second ceramic component and was exposed to post-infiltration heat treatment for fifty hours, was significantly harder than other cermet discs of the same set that were exposed to the heat treatment for shorter time periods. Also, the cermet disc, that included titanium diboride and was exposed to the heat treatment for fifty hours, was significantly harder than the corresponding cermet disc that included only boron carbide.

Therefore, the presence of titanium diboride, as a second ceramic component, prevented the reduction of hardness during prolonged post-infiltration heat treatment that was observed in a cermet that included only boron carbide. Also, the presence of titanium diboride in admixture with boron carbide allowed formation of a hardened cermet that was significantly harder than a cermet exposed to the same conditions but lacking the second ceramic component.

Example IV

Boron carbide powder (ESK specification 1500, manufactured by Eleltroschemeltzwerk Kempten, and having an average particulate size of 3 micrometers) was divided into two portions. One portion was used as received. The other portion was heat treated under argon in a graphite crucible at a temperature of 1800°C for a period of 2 hours. The heat treated powder, after cooling to ambient temperature, was subjected to attrition milling for 2 hours. The milled powder was mixed with the as received portion in water (pH 7). The combined powders were converted to greenware discs and infiltrated as in Example I. The infiltrated discs were heat treated, as in Example I, but at a temperature of 800°C for 10 hours. Results of Vicker's hardness testing, as in Example I, are shown in Table IV.

Table IV

Ceramic Content (by volume)		
Untreated Boron carbide	Heat Treated Boron Carbide	Hardness (Kg/mm2)
100	0	1400
80	20	1120
50	50	1045
20	80	725
0	100	495

The data presented in Table IV show that heat-treated boron carbide can be used as a second, or non-reactive, ceramic component in accordance with the present invention.

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. Such equivalents are intended to be encompassed in the scope of the following claims.

CLAIMS:

1. A process of forming a hardened cermet, comprising the steps of:

a) providing a porous ceramic compact including a first ceramic component and a second ceramic component;

b) at least partially filling pores of the porous ceramic compact with a molten metal component to form a metal-filled ceramic compact;

c) exposing the metal-filled ceramic compact to a sufficient temperature for a sufficient time period to cause at least a portion of the first ceramic component to react with at least a portion of the metal component and form a cermet-hardening component, the second ceramic component undergoing no significant reaction with the molten metal at said temperature; and

d) cooling the metal-filled ceramic compact and cermet-hardening component to room temperature, thereby forming a hardened cermet.

2. A process as claimed in Claim 1 wherein the first ceramic component is present in an amount within a range of between 50% and 95% by volume, based upon total volume of ceramic components in the porous ceramic compact.

3. A process as claimed in Claim 1 wherein the porous ceramic compact is partially densified prior to step (b).

4. A process as claimed Claim 3 wherein the porous ceramic compact has a density within a range of from 50% to 90% of the theoretical density of a combination of the first and second ceramic components.

5. A process as claimed in any one of Claims 1-4 wherein the temperature in step (c) is greater than or equal to one-half of the metal component's melting temperature, but less than the lowest melting or decomposition temperature of the ceramic components, and the time period is within a range of from 0.5 to fifty hours.

6. A process as claimed in any one of Claims 1-4, wherein the first ceramic component is boron carbide and the second ceramic component is titanium diboride or boron carbide that has been heat-treated at a temperature greater than 1800°C but less than 2350°C.

7. A process as claimed in Claim 6, wherein the metal is aluminum or an aluminum-based alloy.

8. A process of forming a hardened cermet laminate comprising the steps of:

a) providing a layered assembly having a first porous ceramic layer and at least one additional porous ceramic layer, the first and additional layers including a first ceramic component and a second ceramic component, each layer within said layered assembly having a ratio of the first ceramic component to the second ceramic component that differs from the ratio within each adjacent layer;

b) at least partially filling pores within each layer with a molten metal component to form a metal-filled layered assembly;

c) exposing the assembly to a sufficient temperature for a time period sufficient to cause at least a portion of the first ceramic component in each layer to react with at least a portion of the metal component contained therein to form a cermet-hardening component, the second ceramic component undergoing no significant reaction with the metal at said temperature; and

d) cooling the assembly resulting from step (c) to room temperature that allows any remaining molten metal to solidify, thereby forming a hardened cermet laminate.

9. A process as claimed in Claim 8 wherein each layer is partially densified prior to step (b) so that it has a density within a range of from 50 to 90% of the theoretical density of a combination of the first and second ceramic components.

10. A process as claimed in Claims 8-9 wherein the temperature in step (c) is greater than or equal to one-half of the metal component's melting temperature, but less than the lowest melting or decomposition temperature of the ceramic components, and the time period is within a range of from 0.5 to 50 hours.

11. A process as claimed in Claim 10 wherein the first ceramic component is boron carbide and the second ceramic component is titanium diboride.

12. A process as claimed in Claim 11 wherein the metal is aluminum or an aluminum-based alloy.

13. A hardened cermet laminate comprising a first hardened cermet layer and at least one additional hardened cermet layer, the first layer containing a first ceramic component, a metal component, at least one product of a reaction between the first and metal components and, optionally, a second ceramic component, each additional layer containing the first and second ceramic components, the metal component and the reaction product, each layer within said laminate having an amount of reaction product and a ratio of first to second component that differs from those of adjacent layers.

14. A hardened cermet as claimed in Claim 13 wherein the first layer has a first component content of 100 percent by volume, based upon total volume of the ceramic components, and five additional layers have respective ratios of first to second components of 90:10, 70:30, 50:50, 30:70 and 10:90.

15. A hardened cermet as claimed in Claims 13-14 wherein the first and second ceramic components are, respectively, boron carbide and titanium diboride and the metal component is aluminum or an aluminum-based alloy.

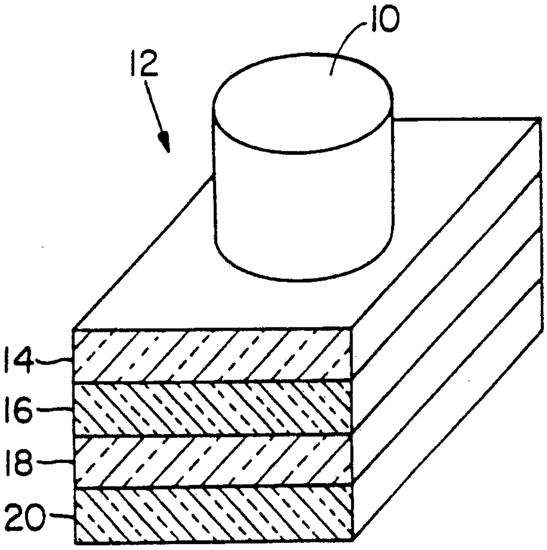

Fig. 1

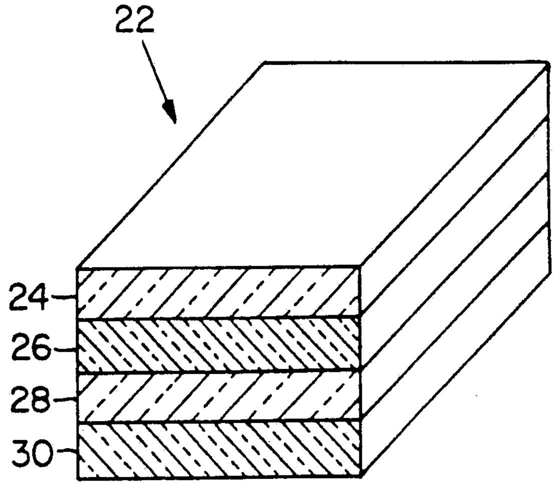

Fig. 2

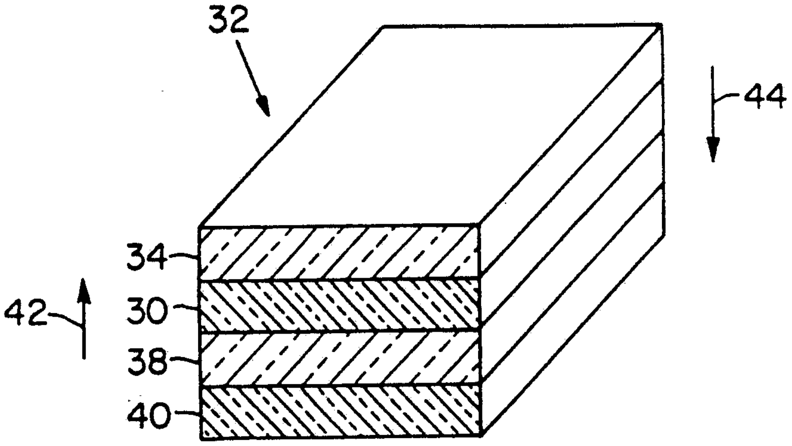

Fig. 3

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/04947

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C22C1/10; B32B18/00; C04B35/65

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C22C ; B32B ; C04B

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
X	EP,A,0 299 905 (LANXIDE TECHNOLOGY COMPANY LP) 18 January 1989	1-7
A	see column 8, line 46 - column 9, line 17; claims 1,2 see column 12, line 1 ---	8,13
A	EP,A,0 369 931 (LANXIDE TECHNOLOGY COMPANY LP) 23 May 1990 see figure 12; example 6 ---	8,13
A	EP,A,0 250 210 (THE REGENTS OF THE UNIVERSITY OF CALIFORNIA) 23 December 1987 see page 5, line 8 - line 14; claim 1; figure 3A -----	8,13

° Special categories of cited documents : [10]

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

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IV. CERTIFICATION

Date of the Actual Completion of the International Search 28 OCTOBER 1992	Date of Mailing of this International Search Report 24. 11. 92
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer Dagmar [illegible]

Form PCT/ISA/210 (second sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9204947 SA 61815

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 28/10/92
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0299905	18-01-89	AU-B- 611697	20-06-91
		AU-A- 1909788	19-01-89
		CN-A- 1031115	15-02-89
		JP-A- 1103945	21-04-89
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		US-A- 5017334	21-05-91
EP-A-0369931	23-05-90	US-A- 5040588	20-08-91
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		JP-A- 2240229	25-09-90
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		DE-A- 3778432	27-05-92
		JP-A- 63053231	07-03-88

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82