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(54) Boron carbide-reactive metal cermets having microstructure tailored by post-densification heat treatment.

(57) Boron carbide-reactive metal cermets can be prepared by consolidating a mixture of boron carbide powder and a particulate source of a metal that reacts with boron carbide to produce dense, soft, cermets in near net shape. The cermets can be hardened to produce a final multiphase microstructure having increased fracture toughness and hardness by a post-denssification heat treatment.

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This invention concerns ceramic-metal composites, also known as cermets, based upon boron carbide and a source of a metal which reacts with boron carbide.

Cermets have properties that differ from those of either the ceramic phase or the metal phase alone. They are conventionally made by powder metallurgical methods, that is, by preparing and mixing individual metal and ceramic powders, pressing the mixed powders into a required shape and subjecting the shape to a sintering heat treatment to bond the particles and develop the required structural integrity, often by direct ceramic-to-ceramic bonding.

Cermets are conventionally used to make engineering components, such as parts of gas turbine or diesel engines, that require mechanical property stability when exposed to rapid temperature changes, strength at operating temperatures and creep resistance. They tend to be less brittle and less prone to formation of extended defects within the material than conventional ceramics.

U.S. Patent 4,556,424 discloses a method of improving the fracture toughness of a hard metal or metal-bound ceramic by exposing it to a heat treating process similar to the transformation toughening of steel. A ceramic composite, such as cobalt-bound tungsten carbide, is first cooled to transform the binder material from a first state to a second state and cause deformation of the binder material. The composite is then heated above ambient temperature to cause the binder material to revert to its first state while retaining some measure of the deformation. The heated composite material is then quenched or subjected to rapid cooling.

U.S. Patent Nos. 4,702,770 and 4,718,941 teach heat treating ceramic precursors infiltrated with a molten metal to tailor the microstructure of boron carbide-reactive metal cermets.

Figure 1 illustrates the post-densification heat treatment of boron carbide containing varying amounts of aluminum at varying temperatures. Figure 2 illustrates post-densification heat treatment of a boron carbide composite containing 30% by volume aluminum showing hardness as a function of heat treatment time and temperature. Figure 3 provides curves showing the effect of heat treatment time on fracture toughness of a boron carbide-aluminum composite which has been subjected to a post-densification heat treatment.

One aspect of the present invention is a boron carbide-aluminum cermet characterized by a boron carbide phase, an aluminum phase and an AlB_2 phase or an Al_4BC phase or an AlB_2 phase and an Al_4BC phase.

A second aspect of the present invention is a boron carbide-reactive metal cermet characterized by a boron carbide phase, a reactive metal phase and a reactive metal boride phase, or a reactive metal boron carbide phase or a reactive metal boride phase and a reactive metal boron carbide phase, the reactive metal being arsenic, barium, beryllium, calcium, cobalt, chromium, iron, hafnium, iridium, lanthanum, lithium, magnesium, manganese, molybdenum, sodium, niobium, nickel, osmium, palladium, platinum, plutonium, rhenium, rhodium, ruthenium, scandium, silicon, strontium, tantalum, technetium, thorium, titanium, uranium, vanadium, tungsten, yttrium or zirconium.

A third aspect is a process for preparing a boron carbide-aluminum cermet comprising:

(a) densifying an admixture of boron carbide powder and aluminum metal powder at a temperature in the vicinity of the melting point of aluminum to produce a densified composite; and

(b) heating the densified composite to a temperature within a range of 450°C to 1000°C for a period of time sufficient to form, within the densified composite, an AlB_2 phase or an Al_4BC phase or an AlB_2 phase and an Al_4BC phase. The time period is within a range of one to fifty hours inclusive.

A fourth aspect is a process for preparing a boron carbide-reactive metal cermet comprising:

(a) densifying an admixture of boron carbide powder and a particulate source of a reactive metal at a temperature in the vicinity of the melting temperature of the reactive metal to procedure a densified temperature the reactive metal being arsenic, barium, beryllium, calcium, cobalt, chromium, iron, hafnium, iridium, lanthanum, lithium, magnesium, manganese, molybdenum, sodium, niobium, nickel, osmium, palladium, platinum, plutonium, rhenium, rhodium, ruthenium, scandium, silicon, strontium, tantalum, technetium, thorium, titanium, uranium, vanadium, tungsten, yttrium or zirconium; and

(b) heating the densified composite to a temperature within a range of 450°C to 1000°C for a period of time sufficient to form, within the densified composite, a reactive metal boride phase or a reactive metal boron carbide phase or a reactive metal phase and a reactive metal boron carbide phase. The time period is within a range of one to fifty hours inclusive.

Powder metallurgy procedures are preferred for preparing densified composites suitable for heat treatment. Powder mixtures may be densified as is, placed in a container before densification or converted to a preform, by a known procedure such as cold pressing, cold isostatic pressing or cold isostatic pressing before densification. The powder mixtures usually contain from 20 to 60 percent by volume of a reactive metal such as aluminum prior to densification. After a post-densification heat treatment, the proportion of metal is from 2 to 12% by volume. The post-densification heat treatment produces a microstructure containing, in addition to the boron carbide and reactive metal phases, a metal boride phase such as AlB_2, or a metal boron carbide phase such as Al_4BC or a metal boride phase and a metal boron carbide phase. Control of the post-densification heat treatment temperature and time allows tailoring of the microstructure. Changes in microstructures vary physical properties of the heat-treated cermets.

The aluminum phase of boron carbide-aluminum cermets may be formed from aluminum metal, aluminum metal alloys or aluminum compounds that are reduced totheir corresponding metal during densification. Boron carbide-aluminum cermets have a number of potential applications or end uses. The applications include, but are not limited to, lightweight structures, cutting tools, spent nuclear fuel containers, radiation resistant structures, hot and cool parts of turbine engines, impact resistant structures, abrasive and wear resistant materials, semiconducting devices, and structures requiring increased thermal shock resistance and a high degree of chemical stability.

Metals that react with boron carbide to form similar boron carbide-reactive metal cermets include arsenic, barium, beryllium, calcium, cobalt, chromium, iron, hafnium, iridium, lanthanum, lithium, magnesium, manganese, molybdenum, sodium, niobium, nickel, osmium, palladium, platinum, plutonium, rhenium, rhodium, ruthenium, scandium, silicon, strontium, tantalum, technetium, thorium, titanium, uranium, vanadium, tungsten, yttrium or zirconium. As with aluminum, the reactive metal phase may be formed from a reactive metal, a metal alloy containing the reactive metal or a reactive metal compound that reduces to its corresponding metal or metal alloy during densification.

The cermets of the present invention result from a process which differs from prior art processes in two aspects. First, densification of :he admixture of boron carbide and the source of aluminum or another reactive metal occurs at a temperature in the vicinity of the melting temperature of the metal. This temperature is believed to minimize the reaction between boron carbide and the aluminum or other reactive metal during densification. Second, the densified admixture or cermet undergoes a heat treatment to produce a microstructure that includes one or more phases other than the boron carbide phase and the reactive metal phase. Variations in the microstructure lead to improvements in physical properties such as fracture toughness or impact strength.

Post-densification heat treatment occurs at a temperature within a range of 450°C to 1000°C. The range is desirably from 500°C to 800°C and preferably from 600°C to 700°C. Heat treatment times fall within a range of from one to 50 hours. The treatment time range is desirably from 1 to 30 hours and preferably from 10 to 20 hours.

Heat treatment temperatures within a range of 600°C to 700°C lead to formation of a reactive metal boride, such as, AlB_2. The boride enhances impact resistance over that of the densified composite prior to heat treatment. As the heat treatment temperature rises above 700°C, a reactive metal boron carbide, such as, Al_4BC begins to form. As the temperature continues to increase, the amount of the reactive metal boron carbide relative to the reactive metal boride also increases. Between 900°C and 1000°C, the reactive metal boron carbide is the dominant reaction product. Heat treatment temperatures in excess of 1000°C cause the reactive metal boride to decompose and generate free reactive metal. Mixtures of the reactive metal boride and the reactive metal boron carbide have fracture toughness and hardness values greater than that of the densified composite prior to heat treatment.

The following examples illustrate various aspects of the invetnion but are not intended to limit its scope. When not otwerwise specified throughout this specification and claims, temperatures are given in degrees centigrade and quarts, percentages, and proportions are by weight.

Example 1

This example illustrates that the properties and chemistry of the B_4C/Al system can be tailored by changing processing conditions. The following powders, processing conditions and characterization methods were used:

The boron carbide was a powder with 21.27% total carbon content, 0.4% free carbon, 1.27% oxygen and a surface area of 6.8 m^2/g. The major impurities were 161 ppm Ca, 142 ppm Cr, 268 ppm Fe and 331 ppm Ni. The aluminum powder, Alcan 105 produced by Alcan-Toyo America, Inc., contained 0.8% Al_2O_3, 0.18% Fe and 0.12% Si and had a surface area of 0.5m^2/g.

A mixture of 70R% by volume boron carbide powder and 30% by volume aluminum powder was mixed and pressed into 24 mm diameter pellets. The pellets were heat-treated for one hour in a mullite tube furnace, in flowing argon, at a temperature within a range of 400°C to 1200°C. The heat-treated pellets were cooled to room temperature either at a rate of 10/minute or by quenching into liquid nitrogen.

Crystalline phases were identified by x-ray diffraction with a Phillips diffractometer using CuK radiation and a scan rate of 2° per minute. The chemistry of all phases was determined from electron probe analysis of polished cross-sections using a CAMECA CAMEBAX electron probe. The accuracy in the determination of elemental composition was better than 3% of the amount present.

The area of the aluminum melting endotherm in the high temperature DSC scan was used as a measure of the reactivity between B_4C and Al at temperatures between 550°C and 1200°C. The data were collected using a Perkin-Elmer DTA 1700 interfaced to a computer. The purge gas was ultra high purity argon flowing at 40 cc/min. The samples were heated in alumina crucibles at 20°C/min and high purity aluminum (99.999%) was used as a standard. The percent aluminum metal was given by A/B x 100, where A is the peak area in cal/g of the Al melt endotherm in the sample and B is the same for the Al standard. Precision and accuracy were 2 percent.

The results show that the reaction between boron carbide and aluminum starts at 450°C with the formation of Al_4BC. The reaction rate is slow below 600°C. In the range of 550° to 600°C, 24% by volume metal (80% of the original Al) can be recovered. Above 600°C, AlB_2 forms and aluminum is rapidly depleted, as illustrated in Figure 1. The open circles in Figure 1 represent the amount of unreacted Al metal retained in a B_4C/Al powder mixture after heating for one hour at temperatures between 450°C and 1200°C, and cooling to room temperature at 10°/minute. The open boxes indicate the amount of unreacted metal present after quenching in liquid nitrogen. Between 600° and 700°C, AlB_2 and B_4C are the predominant phases. Above 700°C, AlB_2 and Al_4BC are present and, as temperature increases, the relative amount of Al_4BC increases. Between 900°C and 1000°C, the dominant reaction product is Al_4BC. At temperatures above 1000°C, AlB_2 decomposes and generates free aluminum. Heat treatment above 1000°C produces mainly $AlB_{24}C_4$ and some Al_4C_3. Phases formed below 1000°C are aluminum rich and their formation leads to the rapid depletion of the metal. Phases formed above 1000°C are boron and carbon rich resulting in B_4C depletion and development composites with larger amounts of free metal and smaller amounts of boron carbide than the same starting powders heated below 1000°C.

The major phases influencing the mechanical properties of B_4C/Al based materials are Al_4BC, AlB_2, $AlB_{24}C_4$ and Al_4C_3. Because the formation of $AlB_{24}C_4$ is associated with the existence of undesirable Al_4C_3, the heat treatment should be limited to temperatures of 1000°C or lower where AlB_2 and Al_4BC are the predominant new phases.

Example 2

Example 2 illustrates that hardness of B_4C/Al cermets can be changed as a function of phase chemistry.

The same powders were used as in Example 1. The boron carbide and aluminum powders were dry mixed in a rotary blender and then pressed into 75 mm diameter discs using uniaxial compaction in a stainless steel die. No lubricants or binders were used. The samples were placed into metal cans. The sealed cans were placed in fluid dies. The fluid dies with mixed B_4C and Al powders were heated in the furnace of Example 1 to 640°C. The fluid dies were then removed from the furnace, placed in a forging press, and compacted. The compacted dies were removed from the forging press and cooled to room temperature. The discs were separated from the cooled dies using conventional procedures and cut into various shapes for testing and characterization.

The bulk hardness was measured on surfaces polished successively with 45, 30, 16, 6 and 1 um diamond paste and finally finished using colloidal silica suspension on a LECO automatic polisher. The Rockwell A hardness was measured using a 13.3 kg load. The Vickers microhardness of isolated phases was measured using a LECO tester and loads of 10 to 20 grams. The largest grains of a particular phase were examined in order to eliminate or minimize the contribution from adjacent or underlying material. Generally, the distance from the center of the indent to the nearest grain boundary was over twice the indent diagonal dimension. The indent diagonals were measured using a scanning electron microscope at 10000X.

After densification, the B_4C/30% by volume Al material had a hardness of 81 in Rockwell A scale. Post-densification heat treatment at 600°C and 1000°C provided a maximum hardness value of 83, which remained stable for extended times as shown in Figure 2. At 1000°C, the hardness declined initially due to the decomposition of AlB_2, but then increased again as Al_4BC was formed. Heat treatments conducted at 700°C, 800°C, 900°C and 1100°C produced a maximum in the hardness versus time curve. At higher temperatures, less time was required to obtain maximum hardness.

The change in hardness is characteristic of the B_4C/Al system and due to the kinetics and B-C-Al phase equilibrium. Below 1000°C, in the initial stage of heat treatment, hard Al_4BC is favored. With increased time, there is insufficient aluminum available and softer AlB_2 forms decreasing overall hardness. Between 600°C and 1000°C Al_4BC and AlB_2 are both present. Increases in the AlB_2/Al_4BC ratio lower the maximum hardness and make the transition from rising to declining hardness more gradual.

After 20 hours of heat treatment, the AlB_2/Al_4BC ratio was 8, 0.7 and 0.4 at 700, 800 and 900°C respectively. At 1100°C, Al_4BC and then $AlB_{24}C_4$ formed resulting in a high hardness composite. However, after 8 to 10 hours of heat treatment, Al_4C_3 became the predominant new phase and the hardness declined. The highest hardness values were achieved through heat treatments of 10 hours at 1100°C (H_{RA}=89), 20 hours 900°C (H_{RA}=88) and 20 hours at 800°C (H_{RA}=88).

Example 3

Example 3 illustrates that fracture toughness of dense B_4C/Al material can be increased. This increase is associated with densification of the metal phase. While the formation of ceramic phases reduces toughness, the extent of this reduction depends on the type of phase formed. AlB_2 is the least detrimental.

The same powders and processing conditions were used as in Examples 1 and 2. Fracture toughness was measured using the Chevron notch technique and standard 4 x 3 x 45 mm samples. The notch was produced with 250 um wide diamond blade and the notch depth to sample height ratio was 0.42. A cross head speed of 0.05mm/minute was used in a 3 point bend fixture. The average of 5 to 7 measurements was reported.

The values of the fracture toughness of many B-C-Al phases are unknown. However, the damage and cracking pattern in the indented phases indicates that AlB_2 has a higher toughness than Al_4BC or $AlB_{24}C_4$. Aluminum containing small ceramic crystals deforms plastically. The damage in AlB_2 represents shear deformation rather than brittle cracking. B_4C and $AlB_{24}C_4$ usually behave similarly, even though, in some cases, the crack propagates through the $AlB_{24}C_4$ and stops at the boron carbide grain boundary. Al_4BC shows brittle behavior with several cracks running from the corners and sides of the indent.

The results in Figure 3 indicate that post-densification heat treatment can substantially improve fracture toughness. The K_{IC} increases over the entire heat treatment range when compared to the pressure densified material. Beyond the maximum at 600°C, K_{IC} decreases. Analytical transmission electron microscopy did not reveal any differences (for example, precipitation) between the pressure densified and heat treated metal phases. However, a reduction in porosity was observed in the heat treated samples implying increased density and improved bonding between the ceramic and metal which would account for the increased fracture toughness. At 600°C, where the highest fracture toughness was obtained, sintering of the metal takes place before significant quantities of new phases are formed. The materials containing AlB_2 have higher K_{IC} values than those with Al_4C and $AlB_{24}C_4$.

Example 4

Example 4 shows that post-densification heat treatment can be used to improve many properties of B_4C/Al cermets by changing the cermet into a multi-phase ceramic material containing only a small amount of residual metal.

It is possible to produce B_4C/Al composites with different phases, but similar amounts of residual unreacted aluminum. The following Table provides data comparing the mechanical properties of the pressure densified and heat treated B_4C/Al composites. The highest hardness and modulus were obtained in samples containing Al_4BC . While these materials had improved toughness relative to the pressure densified materials, it was only 8.2 MPa $m^{1/2}$. On the other hand, samples AlB_2 containing AlB_2 exhibited increased fracture toughness (9.2 MPa $m^{1/2}$), but only slight hardness (from 81 to 85) improvement.

Because the AlB_2/Al_4BC ratio can be changed and controlled by heat treatment at a temperature between 700°C and 900°C, the properties of B_4C/Al composites canbe selected for a specific application. Processing at 1000°C or below allows the formation of large amounts of AlB_2 and avoids the formation of Al_4C_3.

In heat treating at or below 600°C, the new phases form in limited amounts and a multi-phase ceramic is not produced. The resultant B_4C/Al cermets are characterized by a microstructure of isolated boron carbide grains in an aluminum matrix with improved fracture toughness and fracture strength.

TABLE - The effect of heat treatment on properties of B_4C/Al materials with isolated boron carbide in a metal matrix.

Property	After pressure densification	After Heating above 600°C to produce:			After Heating at 600°C
		AlB_2	Al_4BC	$AlB_{24}C_4A$	
Density g/cm^3	2.57	2.63	2.70	2.62	2.58
Flexure strength (MPa)	419	357	351	312	434
Fracture toughness (MPA m$^{1/2}$)	7.23	9.2	8.2	7.5	12.7
Young modulus (GPa)	254	290	310	280	260
Bulk modulus (GPa)	138	167	175	156	140
Hardness Rockwell A	81	85	88	88	81
Poissons's ratio	0.23	0.21	0.20	0.20	0.23

While this invention has been described with reference to certain specific embodiments, it will be recognized by those skilled in the art that many variations are possible without departing from the scope and spirit of the invention and it will be understood that it is intended to cover all changes and modifications of the invention, disclosed herein for the purposes of illustration, which do not constitute departures form the spirit and scope of the invention.

Claims

1. A cermet of boron carbide and a reactive metal, and having a boron carbide phase, a reactive metal phase, and either or both of a reactive metal boride phase and a reactive metal boron carbide phase, wherein the reactive metal is aluminum, arsenic, barium, beryllium, calcium, cobalt, chromium, iron, hafnium, iridium, lanthanum, lithium, magnesium, manganese, molybdenum, sodium, niobium, nickel, osmium, palladium, platinum, plutonium, rhenium, rhodium, ruthenium, scandium, silicon, strontium, tantalum, technetium, thorium, titanium, uranium, vanadium, tungsten, yttrium or zirconium.

2. A cermet as claimed in Claim 1, wherein said reactive metal is present in an amount of from 2 to 12% by volume.

3. A cermet as claimed in Claim 1 or Claim 2, wherein the reactive metal is aluminum and wherein the cermet comprises a boron carbide phase, an aluminum phase, and either or both of an AlB_2 phase and an Al_4BC phase.

4. A process for preparing a cermet of a reactive metal with a boron carbide comprising:-
   (a) densifying a mixture of boron carbide powder and a particulate source of the reactive metal at a temperature in the vicinity of the melting temperature of the reactive metal to produce a densified composite, wherein the reactive metal is aluminum, arsenic, barium, beryllium, calcium, cobalt, chromium, iron, hafnium, iridium, lanthanum, lithium, magnesium, manganese, molybdenum, sodium, niobium, nickel, osmium, palladium, platinum, plutonium, rhenium, rhodium, ruthenium, scandium, silicon, strontium,

tantalum, technetium, thorium, titanium, uranium, vanadium, tungsten, yttrium or zirconium; and
(b) heating the densified composite to a temperature from of 450°C to 1000°C for a period of time sufficient to form within the densified composite a reactive metal boride phase or a reactive metal boron carbide phase or both.

5. A process as claimed in Claim 4, wherein the reactive metal is aluminum and the densified composite comprises an AlB_2 phase or an Al_4BC phase or both.

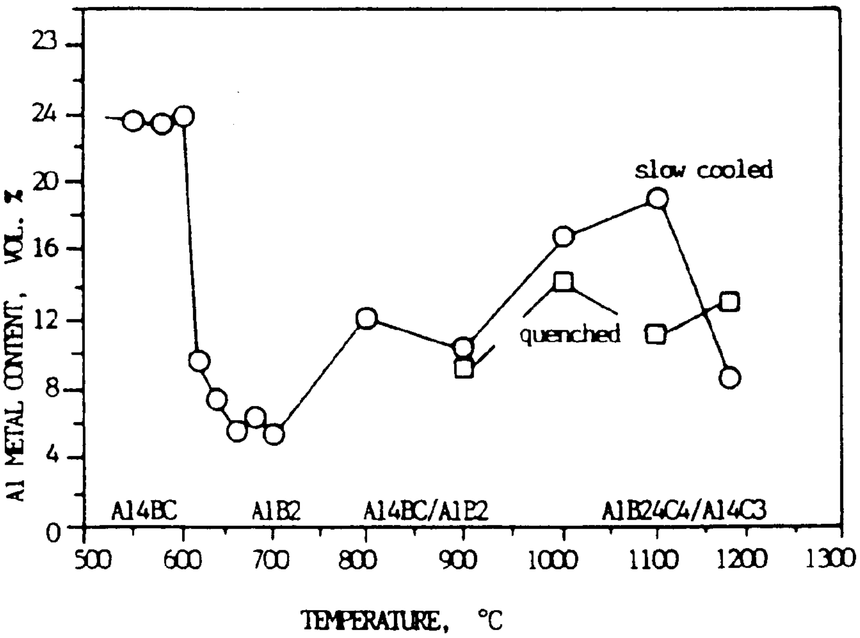
6. The process of Claim 4 or Claim 5, wherein, prior to heating, the densified composite comprises from 20 to 60% by volume of the reactive metal, and 80 to 40% by volume boron carbide.

7. The process of any one of Claims 4 to 6, wherein, after heating, the densified composite contains from 2 to 12% by volume aluminum.

8. The process of any one of Claims 4 to 7, wherein the densified composite is heated to a temperature of from 500°C to 800°C for a period of from 10 to 30 hours.

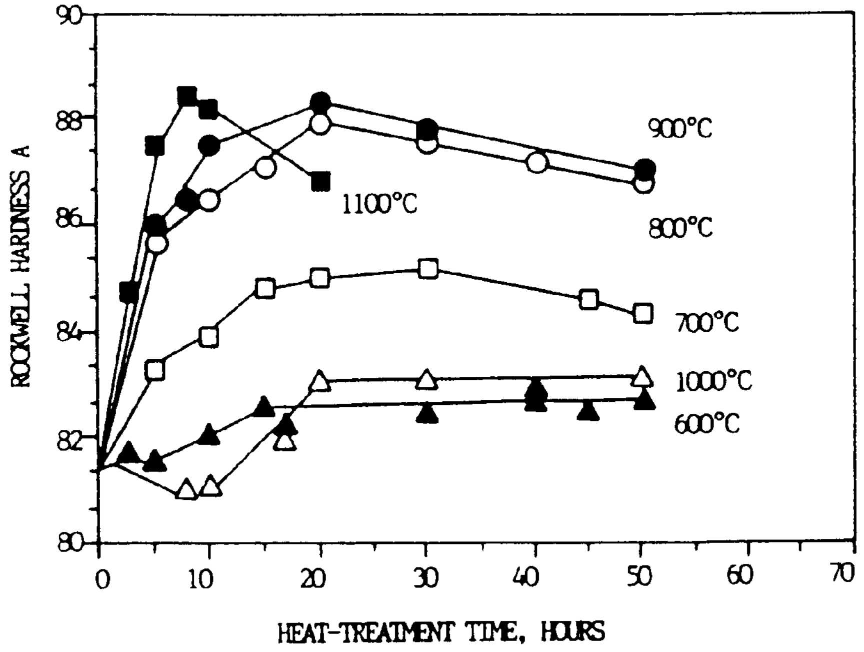
9. The process of Claim 8, wherein the densified composite is heated to a temperature of from 600°C to 700°C for a period of from 10 to 20 hours.

Fig-1



BORON CARBIDE/ALUMINUM COMPOSITES CONTAINING VARYING AMOUNTS OF ALUMINUM HEAT TREATED AT VARYING TEMPERATURES.

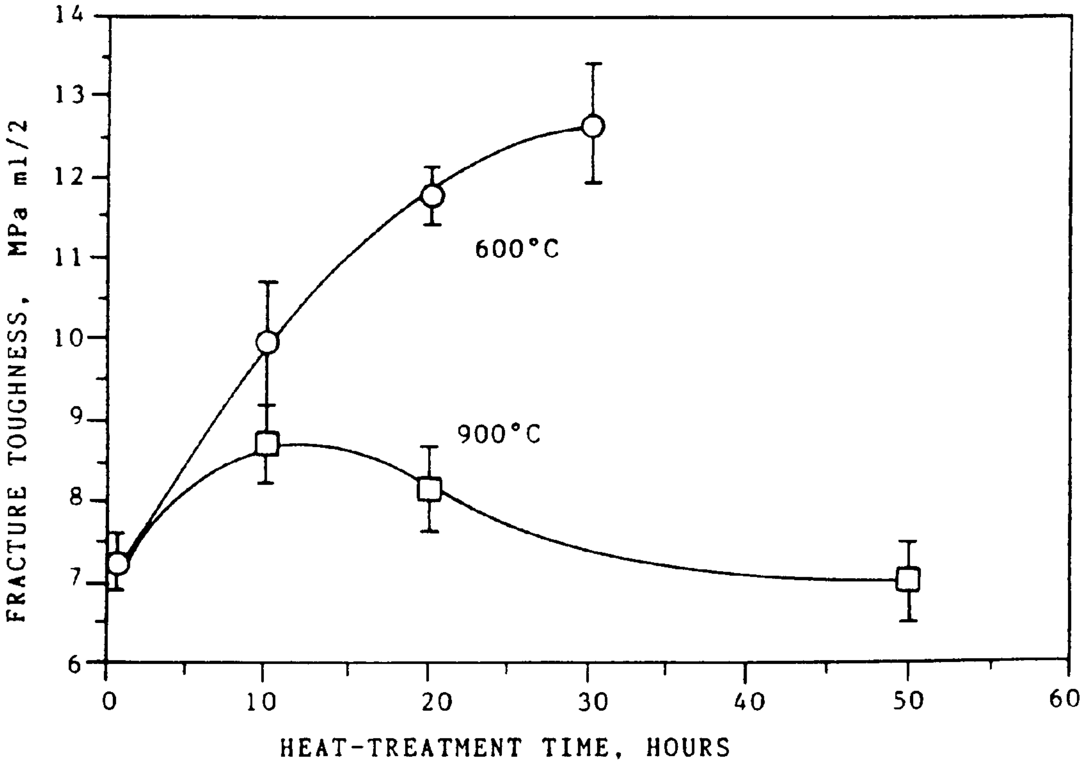
Fig-2



BORON CARBIDE/ALUMINUM COMPOSITE CONTAINING 30% BY VOLUME ALUMINIUM

Fig-3

THE EFFECT OF HEAT-TREATMENT TIME ON FRACTURE TOUGHNESS OF B4C/AL BASED MATERIALS



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EUROPEAN SEARCH REPORT

Application Number

EP 91 30 9628

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-4 605 440 (HALVERSON ET AL.) * column 2, line 21 - line 30; example 1 * ---	1-8	C22C1/05 C22C29/00 C04B41/51
X	EP-A-0 378 504 (LANXIDE TECHNOLOGY COMPANY,LP) * claims 1,4 * ---	1	
A,D	WO-A-8 700 557 (WASHINGTON RESEARCH FOUNDATION) & US-A-4 702 770 ---		
A,D	EP-A-0 250 210 (THE REGENTS OF THE UNIVERSITY OF CALIFORNIA) & US-A-4 718 941 -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C22C C04B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	24 JANUARY 1992	ASHLEY G.W.

CATEGORY OF CITED DOCUMENTS

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