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<p>(21) International Application Number: PCT/US86/00779 (22) International Filing Date: 16 April 1986 (16.04.86) (31) Priority Application Number: 727,456 (32) Priority Date: 26 April 1985 (26.04.85) (33) Priority Country: US</p> <p>(71) Applicant: MARTIN MARIETTA CORPORATION [US/US]; 6801 Rockledge Drive, Bethesda, MD 20817 (US).</p> <p>(72) Inventors: CHRISTODOULOU, Leontios ; 117 Ingle- side Avenue, Baltimore, MD 21228 (US). NAGLE, Dennis, Charles ; 10148 Tanfield Court, Ellicott City, MD 21043 (US). BRUPBACHER, John, Michael ; 23 Delrey Avenue, Baltimore, MD 21228 (US).</p>		<p>(74) Agents: MYLIUS, Herbert, W. et al.; Martin Marietta Corporation, 6801 Rockledge Drive, Bethesda, MD 20817 (US).</p> <p>(81) Designated States: AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, SE (European patent), SU.</p> <p>Published <i>With international search report.</i></p>
<p>(54) Title: ALUMINUM-CERAMIC COMPOSITES</p> <p>(57) Abstract</p> <p>Metal-ceramic composites of aluminum or aluminum alloy materials, having discrete finely dispersed particles of ceramic materials such as TiB₂, provide strengthened and hardened materials having improved fatigue, elongation, and elastic modulus characteristics.</p>		

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ALUMINUM-CERAMIC COMPOSITES

Background of the Invention

The present invention relates to a composite material comprising ceramic material in an aluminum matrix, wherein the ceramic comprises a boride, carbide, oxide, nitride, silicide, etc., of one or more metals other than the aluminum matrix. The matrix metal, moreover, may constitute an alloy of aluminum.

For the past several years, extensive research has been devoted to the development of metal-ceramic composites, such as aluminum reinforced with carbon, boron, silicon carbide, silica, or alumina fibers, whiskers, or particles. Metal matrix composites with excellent high temperature yield strengths and creep resistance have been fabricated by the dispersion of very fine (less than 0.1 micron) oxide or carbide particles throughout the metal or alloy matrix. The production of such dispersion-strengthened composites is conventionally accomplished by mechanically mixing metal powders of approximately 5 micron diameter or less with the oxide or carbide powder (preferably 0.01 micron to 0.1 micron). High speed blending techniques or conventional procedures such as ball milling may be used to mix the powder. Standard powder metallurgy techniques are then employed to form the final composite. Conventionally, however, the ceramic component is large, i.e. greater than 1 micron, due to a lack of availability, and high cost, of such small particle size materials. Further, in many cases where the particulate materials are available in the desired size, they are extremely hazardous due to their pyrophoric nature.

Alternatively, molten metal infiltration of a ceramic mat has been used to produce composites. In some cases elaborate particle coating techniques have been developed to protect ceramic particles from molten metal during molten metal infiltration.

- 2 -

Techniques such as this have resulted in the formation of silicon carbide-aluminum composites, frequently referred to as SiC/Al, or SiC aluminum. This approach is suitable for large particulate ceramics (e.g. greater than 1 micron) and whiskers. The ceramic material, such as silicon carbide, is pressed to form a compact, and liquid metal is forced into the packed bed to fill the interstices. Such a technique is illustrated in U.S. Patent 4,444,603, of Yamatsuta et al, issued April 24, 1984.

The presence of oxygen in ball-milled powders used in the prior art metallurgy techniques, or in molten metal infiltration, can result in oxide formation at the interface of the ceramic and the metal. The presence of such oxides will inhibit interfacial binding between the ceramic phase and the matrix, thus adversely effecting ductility of the composite. Such weakened interfacial contact can also result in reduced strength, loss of elongation, and crack propagation.

Internal oxidation of a metal containing a more reactive component has also been used to produce dispersion strengthened metals, such as internally oxidized aluminum in copper. For example, when a copper alloy containing about 3 percent aluminum is placed in an oxidizing atmosphere, oxygen may diffuse through the copper matrix to react with the aluminum, precipitating alumina. This technique, although limited to relatively few systems, has offered a preferred method for dispersion hardening.

In U.S. Patent 2,852,366, of Jenkins, it is taught that up to 10 percent by weight of a metal complex can be incorporated into a base metal or alloy. The patent teaches blending, pressing, and sintering a mixture of a base metal, a base metal compound of the non-metallic complexing element, and an alloy of the base metal and the complexing metal. Thus, for example, the reference teaches mixing powders of nickel, a nickel-titanium alloy, and a nickel-boron alloy, pressing, and sintering the mixed powders to form a coherent body in which a stabilizing unprecipitated "complex" of titanium and boron is dispersed in a nickel matrix. Precipitation of the complex phase is specifically avoided.

- 3 -

In recent years, numerous ceramics have been formed using a process referred to as self-propagating high-temperature synthesis (SHS), which involves an exothermic, self-sustaining reaction which propagates through a mixture of compressed powders.

5 Generally the SHS process takes place at super atmospheric pressures, and is ignited by electrical impulse, thermite, or spark. The SHS process involves mixing and compacting powders of the constituent elements, and igniting the green compact with a suitable heat source. On ignition, sufficient heat is released to

10 support a self-sustaining reaction, which permits the use of sudden, low power initiation of high temperatures, rather than bulk heating over long times at lower temperatures. Exemplary of these techniques are the patents of Merzhanov et al. In U.S. Patent 3,726,643, there is taught a method for producing

15 high-melting refractory inorganic compound by mixing at least one metal selected from groups IV, V, and VI of the Periodic System with a non-metal such as carbon, boron, silicon, sulfur, or liquid nitrogen, and heating the surface of the mixture to produce a local temperature adequate to initiate a combustion process. In

20 U.S. Patent 4,161,512, a process is taught for preparing titanium carbide by ignition of a mixture consisting of 80-88 percent titanium and 20-12 percent carbon, resulting in an exothermic reaction of the mixture under conditions of layer-by-layer combustion. These references deal with the preparation of ceramic

25 materials, absent the presence of a binder.

Similarly, U.S. Patent 4,431,448 teaches preparation of a hard alloy by intermixing powders of titanium, boron, carbon, and a Group I-B binder metal, such as copper or silver, compression of the mixture, local ignition thereof to initiate the exothermic

30 reaction of titanium with boron and carbon, and propagation of the ignition, resulting in an alloy comprising titanium diboride, titanium carbide, and the binder metal. This reference, however, is limited to the use of Group I-B metals such as copper and silver as binders, and requires local ignition. Products made by

35 this method have low density, requiring subsequent compression and compaction.

- 4 -

European Patent Publication No. 0115688, of Corning Glass Works, published August 15, 1984, relates to cermet bodies formed by reaction sintering of stoichiometric mixtures of reactants. The reference teaches formation of bodies comprising 30-95 mole percent of a non-oxide ceramic compound, and 5-70 mole percent of a metal or alloy. The method taught is limited to reaction sintering of premixed and shaped particulate reactants, said reactants preferably having a maximum particle size substantially less than 44 microns. In such a reaction sintering, normally conducted at superatmospheric pressures for time periods of hours, the metal matrix material is a product of the reaction of ceramic forming reactants.

Australian Patent Application 22960/83, published July 5, 1984, discloses cermet materials comprising a minor proportion of ceramic in a metal matrix, characterized by the ceramic forming an open-cell continuous network, the interstices of which are filled with metal. The reference fails, however, to provide a composite comprising discrete, evenly distributed, and separate ceramic particles in a metal matrix, and in fact would appear to advocate the presence of a ceramic matrix.

In Application Serial No. 662,928 filed October 19, 1984, by the present inventors, a process is disclosed for the in-situ precipitation of ceramic materials in a metallic matrix, utilizing a solvent assisted/activated reaction wherein the matrix metal is a solvent for the ceramic forming constituents. The specific metal matrices suitable for the process disclosed therein include aluminum, and alloys thereof, as well as a variety of other metals, and alloys. The reaction set forth by said Application Serial No. 662,928 is the preferred means for preparation of the composite structures of the present invention.

Summary of the Invention

It is an object of the present invention to provide inexpensive composite materials, consisting of discrete finely dispersed particulate ceramic materials, precipitated in-situ in aluminum, or alloys of aluminum.

- 5 -

It is a further object of this invention to provide dispersion hardened metals and alloys. It is a particular object of this invention to provide a composite comprising submicron titanium diboride particulates in an aluminum matrix.

5 The composite of the present invention may preferably be formed by the in-situ precipitation of up to about 95 percent by weight of a ceramic material in an aluminum matrix, wherein the ceramic comprises a boride, carbide, oxide, nitride, silicide, aluminide, selenide, sulfide, or germanide, of a metal other than
10 the solvent matrix metal. It has been found that by mixing the constituents or elements of the desired ceramic material with the solvent matrix metal, and heating to a temperature at which substantial diffusion and/or solvation of the reactive elements in the matrix can occur, typically close to the melting point of the
15 solvent matrix metal, a solvent assisted/activated reaction, which is generally exothermic, can be initiated. This solvent assisted/activated reaction results in the extremely rapid formation and dispersion of finely divided particles of the ceramic material in the metal matrix. While this invention may be
20 associated with pure aluminum systems, it is also applicable to alloys thereof.

Brief Description of Drawings

Figure I sets forth a graphic comparison of fatigue test results for a conventional aluminum alloy and a similar alloy in
25 accord with the present invention.

Figure II demonstrates comparative hardness measurements of the same two alloys under varying aging conditions.

Description of Preferred Embodiments

The present invention is particularly directed to a novel
30 composition of fine particulate ceramics, discretely dispersed within aluminum and/or aluminum alloy systems, said composite having enhanced mechanical properties, such as high elastic modulus, (Young's Modulus), Shear Modulus, Rockwell B hardness,

- 6 -

Knoop hardness, decreased beam bend deformation, greater thermal shock resistance, high-temperature stability, and improved wear resistance. However, while the ceramic particles are preferably submicron in diameter, larger particles of the ceramic material
5 may be present in the aluminum matrix, up to the point at which such larger particles result in component embrittlement, or loss of ductility, etc. Such improved properties as attained by the present invention offer weight savings in stiffness limited applications, higher operating temperatures and associated energy
10 efficiency improvements, and reduced wear in parts subject to abrasion and/or erosion. A specific application of such materials is in the construction of turbine engine components, such as blades.

Exemplary of suitable ceramic precipitates are the borides,
15 (including diborides), carbides, oxides, nitrides, silicides, aluminides, selenides, sulfides, and germanides. Suitable elements include all of the elements which are reactive to form ceramics, including, but not limited to, transition elements of the third to sixth groups of the Periodic Table. Particularly
20 useful ceramic-forming constituents include aluminum, titanium, silicon, boron, molybdenum, tungsten, niobium, vanadium, zirconium, chromium, hafnium, yttrium, cobalt, nickel, and iron. Additional elements suitable for inclusion as ceramic constituents include magnesium, carbon, selenium, tantalum, gallium, manganese,
25 germanium, zinc, arsenic, antimony, lithium, and thorium.

As the matrix metal, or solvent metal, one may use aluminum or any alloy thereof capable of dissolving or sparingly dissolving the precursors of the ceramic phase, and having a lesser capability for dissolving the ceramic precipitate. Thus, the
30 matrix aluminum acts as a solvent for the reaction species, but not for the desired ceramic precipitate. It is to be noted that the matrix aluminum acts primarily as a solvent in the preferred formation technique utilized to prepare the composites of the present invention, and that the constituents of the ceramic
35 precipitate have a greater affinity for each other than either has for the solvent metal.

- 7 -

When aluminum alloys are utilized, one may retain the beneficial properties of said alloys, and increase the modulus of elasticity, high temperature stability, and wear resistance, although some loss of ductility may be encountered in certain soft alloys. For example, 7075 aluminum alloy, containing from about 5 percent to about 40 percent by weight titanium diboride, responds to age-hardening in the same fashion that the 7075 alloy alone does, but exhibits a substantial increase in modulus of elasticity, higher temperature capability, greater high temperature stability, and extremely high wear resistance. Further, the composites of the present invention may be fabricated in conventional fashion, by forging, extruding, rolling, machining, etc.

Varying amounts of ceramic may be incorporated into the composite material, depending upon the end use and the properties desired in the product. For instance, for dispersion strengthened alloys having high modulus, one may utilize a preferred range of from about 5 percent by volume to about 25 percent by volume. However, the ceramic volume fraction for dispersion strengthening may be varied considerably, so as to produce a composite with the desired combination of properties, within the range of from about 0.5 percent by volume up to the point at which ductility is sacrificed to an unacceptable extent. For example, the presence of more than about 25 percent by volume of ceramic can result in loss of elongation in some matrices.

In contrast, cermets of up to about 95 percent or more by volume of ceramic material in the metal matrix may be produced. The primary determining factors in the utilization of such materials as cutting tools will be the wear, gouging, and chipping resistances of the composite material produced. Preferred ranges for cermet materials will, of course, be dependent upon the desired end use. It is possible to effectively tailor the composition to achieve any desired properties by controlling the proportions of the reactant and solvent materials. For instance, the modulus of elasticity may be approximated by the "Rule of Mixtures" such that the appropriate proportions of starting

- 8 -

materials are employed. As indicated, composites in accordance with the present invention may comprise from as little as about 0.5 percent ceramic phase to about 95 percent ceramic. Composites having from about 5 percent to about 25 percent ceramic are suitable for all structural applications, as well as exhibiting favorable hardness and wear resistance characteristics. Those composites comprising more than about 25 percent and less than about 60 percent ceramic are suitable for structural applications which are subject to compression loading and do not require elongation. Moreover, those composites having greater than about 25 volume percent ceramic are suitable for applications in which wear resistance is paramount, with composites of from about 60 percent to about 95 percent by volume ceramic being most suitable for cutting tools or abrasion resistant surfaces.

A comparison of various properties of a composite made in accordance with the present invention with those of a conventional aluminum alloy is shown in Table I. As can be seen, an improvement of about 30 percent in modulus of elasticity is achieved with retention of an acceptable level of ductility.

20

TABLE I

25

30

Material	Hardness Rockwell B	Modulus of Elasticity 10^6 lbs/in ²	Elongation %
7075 Al	75	10.3	7.0
7075-15 vol% TiB ₂ (Forging)	90-100	13.2	4.0

It is noted that the aluminum-ceramic composites of the present invention have a number of advantages over prior art materials such as silicon carbide-aluminum. For example, these composites are considerably less expensive and more convenient to

- 9 -

manufacture, have more uniform dispersion of the particulate material in the matrix metal, and are not subject to oxide formation at the aluminum/ceramic interface. Moreover, the composites of this invention are isotropic materials, having equal or essentially equal properties in all planar directions. This differs from hot-pressed composites, which are anisotropic due to the unidirectional pressing forces exerted during their formation. In addition, the composite materials of the present invention are readily castable to near-net shape, whereas prior art composite materials have not been castable or readily formed. The product composites also have improved properties, such as superior hardness and modulus, improved high temperature stability and processibility, without significant degradation of properties such as fracture toughness or ductility.

Aluminum-titanium diboride composites of the present invention, for example, attain high wear resistance and Young's Modulus, with no loss of fracture toughness. Silicon carbide-aluminum having a similar elastic modulus exhibits significantly lower toughness values, and would in fact be subject to brittle failure.

As illustrated in Figure I, the fatigue properties (crack growth rate per cycle) of the aluminum composites of the present invention are better than those of similarly heat treated base alloy (without particulate inclusion). This indicates that the inventive composites are less subject to fatigue failure than base alloys having the same heat treatment.

It has also been found that a composite of the present invention having almost twice the elastic modulus of the base alloy metal maintains surprising ductility. The combination of improved elastic modulus and elongation achieved by the present composites is unavailable in prior art materials, and is believed to be due to the very small (less than 1 micron in preferred embodiments) particle size and even distribution of the precipitated phase. It must be noted that similar composites, produced by classical powder metallurgy techniques, do not yield

- 10 -

the same combination of properties. Thus, while the same hardness may be achieved, similar elongation will not be achieved, due to matrix-oxide contamination weakening of the bond between the metal matrix and the ceramic particle. Composites of the present invention provide moduli of elasticity ranging from that of the base matrix to that of the incorporated ceramic, dependent upon the volume fraction and shape of the ceramic phase. For example, based on The Rule of Mixtures, 20 volume percent TiB_2 in aluminum would have a modulus of approximately 22×10^6 psi, while the base metal modulus would be approximately 10×10^6 psi. On the other hand, the same composite materials exhibit elongations unexpectedly greater than about 1 percent, and preferably about 3 to 4 percent or more. It is also recognized that small particle size is desirable when seeking high fracture toughness and/or high elongation.

Table II demonstrates the comparability of aluminum alloy 2024 T6 with composites of the present invention (2024XD T6) subjected to slightly lower heat treatment temperatures. Whereas the Aluminum Association standards call for a $920^{\circ}F$. solution heat treatment of the 2024 T6 alloys, it appears that the composite materials benefit from a slightly (approximately $20^{\circ}F$.) lower heat treatment temperature.

- 11 -

Table II

	Material	Yield (KSI)	Ultimate (KSI)	Elongation (%)
5	2024 T6*	50	64	5
	2024XD T6	47.6	60.0	4.8
	(885°F Solution Heat Treat)	46.5 47.4	61.2 60.8	6.5 4.9
10		49.0	60.3	4.4
		48.9	60.0	4.9
	2024XD T6	46.9	62.2	4.7
	(890°F Solution Heat Treat)	48.3 47.6	61.6 62.4	4.7 4.1
15		----	63.5	5.2
		46.9	64.2	6.3
	2024XD T6	49.4	66.5	5.3
20	(900°F Solution Heat Treat)	44.9 46.9	60.2 66.8	3.1 **
		44.9	60.1	**

* - Aluminum Association Standards and Data, 1982, p. 107.

25 ** - Fracture Outside Gage Length.

Wear test data, as set forth in Table III, indicate a very significant improvement in durability in both heat treated (HT) and non-treated composites of the present invention as compared to the base alloy.

Table IIIWEAR TEST DATA

ALL TEST RUN AT 100 RPM, 220 SiC GRIT,
0.2 HRS., UNDER 3301.3 GMS. LOAD

	SAMPLE	VOL. (CM ³)	Wear Rate (HR/CM ³)
5	6061	0.350	0.57
	6061 XD	0.032	6.45
10	6061 XD	0.033	6.06
	2014	0.332	0.60
	2014 XD	0.009	22.2
	2014 XD(H.T.)	0.009	22.2
	7075	0.295	0.68
15	7075 XD	0.008	25.0
	7075 XD(H.T.)	0.007	28.6

Rockwell B hardness of composites of the present invention has been found to be very similar to that of the base alloy employed, as illustrated in Figure II.

20 It is to be noted that care must be taken to avoid the presence of inclusions or particulate impurities such as carbon, refractory brick, or oxides. Such inclusions may lead to brittle behavior by initiating fracture.

25 Other properties of the aluminum-ceramic composites of the present invention demonstrate values at least equivalent to those of the base alloy utilized. These properties include Young's Modulus, shear modulus, high temperature stability, corrosion resistance, thermal shock resistance, thermal coefficient of expansion, and beam deflection.

- 13 -

The aluminum-ceramic composites may be easily fabricated by conventional techniques, such as extrusion, rolling, and forging. The composites may be precision cast, since the precipitated particulate phase is so fine and so evenly distributed as to
5 permit the retention of fluidity by the matrix metal phase. Also, due to the inertness of the particulate phase, and its insolubility in the matrix metal, weldability of the composites is significantly enhanced, particularly when compared to prior art materials such as silicon carbide-aluminum.

10 Various reaction modes have been identified for preparation of the composites of the present invention. In one mode, the starting materials constitute individual powders of each of the solvent metal and the individual constituents of the ceramic to be formed. For example, one may react a mixture of aluminum,
15 titanium, and boron, to form a dispersion of titanium diboride in an aluminum matrix.

In a second reaction mode, one may react individual alloys of a common metal, one such alloy comprising an alloy of aluminum with one of the constituents of the ceramic, and the other
20 comprising an alloy of aluminum and the other constituent of the ceramic. As an example, one may react a mixture of aluminum-titanium alloy with aluminum-boron alloy, to form a dispersion of titanium diboride in aluminum. This alloy-alloy reaction route may, in some cases, be relatively slower than the
25 elemental route, yet may offer economic advantages because the alloys utilized can be cheaper than the elemental powders. In this case, the preferred technique is that of separately melting master alloys containing the chosen elements and mixing them in the molten state, forming a mass in which the dissolved aluminum
30 acts as a liquid solvent for the constituents of the ceramic.

A third reaction mode constitutes a combination, or intermediate, of the first two modes discussed above. Thus, one may react a premixed alloy of aluminum and one reactive species, with an elemental powder of the second reactive species, such as
35 combining an aluminum-titanium alloy with elemental boron powder. This reaction mode may be relatively more expensive than the

- 14 -

alloy-alloy reaction mode, but offers a more rapid reaction, which in turn permits formation of finer grain precipitates than obtainable by the alloy-alloy route. However, the alloy-elemental powder reaction mode could be relatively less expensive, although slower, than the elemental powder mode, in most cases.

It is also to be noted that complex compounds, as well as plural ceramic phases, may be precipitated. Thus, aluminum matrix combinations with complex ceramics such as titanium zirconium boride, may be prepared.

It is particularly to be noted that the prior art teaches that the combination of elemental powders, particularly of a coarse particulate size, would yield undesirable compounds, or large agglomerated aggregates. In contrast, the present invention provides for the formation of finely dispersed precipitate in a matrix of the aluminum. It is important that the ceramic precipitate material is not soluble in the aluminum, while the constituents of the ceramic, individually, are at least sparingly soluble in aluminum. Thus, the exothermic dispersion reaction mechanism depends upon a certain amount of each ceramic forming constituent dissolving and diffusing in the aluminum, and while in solution (either liquid or solid state), reacting exothermically to form the insoluble ceramic, which precipitates rapidly as a very fine particulate. The aluminum, functioning as a solvent, provides a medium in which the reactive elements may diffuse and combine. Once the initial reaction has occurred, the heat released by the exothermic reaction causes additional diffusion of reactive components in the solvent aluminum, and drives the reaction to completion.

A mixture constituting 22 percent titanium, 10 percent boron, and 68 percent aluminum powders was placed in a crucible, and placed in a furnace which was heated to 735°C. Temperature readings were obtained by a thermocouple placed near the specimen, and represent minimum temperatures attained. A plateau exists on the temperature trace obtained, indicating absorption of energy, attributable to localized melting, and the initiation of

- 15 -

substantial diffusion of the reactive components. The temperature trace then indicated the solvent assisted initiation of the reaction of the reactive constituents, and the very rapid temperature increase associated therewith. As shown by the
5 temperature trace, extremely high temperatures were achieved in very short periods of time. During this time frame, essentially all of the reactive components in the solvent metal reacted to form the insoluble ceramic, which immediately precipitated, as submicron discrete particulates.

10 The cool-down period following initiation of the reaction and consumption of the reactive constituents is believed important in achieving very small grain size, and limiting grain growth. It is known that at high temperatures, it is possible for the ceramic particles to grow, e.g. by agglomeration. This should also be
15 avoided, because of the negative effect of large particle sizes on ductility. The cool-down or quenching of the reaction is, in a sense, automatic, since once the ceramic forming constituents are completely reacted, there is no further energy released to maintain the high temperatures achieved. However, one may control
20 the rate of cool-down to a certain extent by control of the size and/or composition of the mass of material reacted. That is, large thermal masses absorb energy, and cool down more slowly, thus permitting growth of larger particles, such as may be desired for greater wear resistance, e.g. for use in cutting tools. It is
25 recognized that if it is desired to rapidly cool the reaction mass to an intermediate temperature, one may achieve this by the introduction of a stream of cool inert gas, such as helium. Thus, the temperature may be rapidly reduced from the maximum temperature attained to a temperature where grain growth is
30 minimal. In terms of temperatures that cause coarsening of the particle size, temperatures in the region of 1000°C are not generally believed to have substantial impact on particle growth. However, at temperatures in the region of 1600°C and higher, grain growth can occur over extended time periods. For example, silicon nitride may begin to grow at 1600°C, over a period of days,

- 16 -

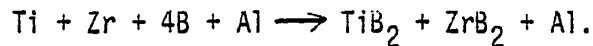
whereas titanium diboride will not begin to exhibit grain growth below about 1800°C. The incidence of particle growth will depend on the particular ceramic phase being formed.

Further, slowly cooling the reaction product is in some cases
5 advantageous, since rapid quenching of some ceramic-aluminum composites as are formed by this invention may result in a high incidence of fracturing due to thermal stresses.

The reaction temperature has generally been found to be relatively close to the melting temperature of aluminum in liquid
10 state reactions. For example, in the production of titanium diboride in aluminum, the reaction proceeds at a temperature around 650°C, or very close to the melting point of the aluminum solvent. It should be noted that in the absence of a solvent
15 metal, the reaction of titanium and boron to form titanium diboride was not observed to proceed below a temperature of about 1200°C, and generally will produce large crystallites having a particle size at least as large as the starting materials. While
20 one need not actually reach the melting temperature, one must achieve a temperature where localized or incipient melting occurs, or a state where substantial diffusion of the reactive species in the aluminum can occur.

It is noted that with respect to impurities, the aluminum may be alloyed at will, while in the reactive constituents, a limited
25 amount of alloying element or impurity may be tolerated. It has been found that an impurity with which a reactive constituent forms a stable compound may not exceed approximately 10 percent by volume. For example, the presence of magnesium in boron appears to inhibit the formation of titanium diboride in an aluminum
30 matrix by forming a magnesium-boron complex on the surface of the boron particles, thereby limiting diffusion of the boron in the matrix. The presence of magnesium in the aluminum, however, does not appear to have this effect. That is, boride forming materials in the boron itself will inhibit the desired dissolution or diffusion of the boron and its subsequent reaction to form titanium diboride.

It is also to be noted that in accordance with the present invention, one may have composites formed by the complex precipitation of a plurality of systems. There is no real limit on the number of ceramic phases which can be precipitated. Thus, it is possible to have composites having complex ceramic phases, such as $Ti(B_{0.5}C_{0.5})$, or alternatively, to a mixture of titanium diboride and zirconium diboride in an aluminum matrix, precipitated in accordance with the reaction:



It has been found that the particle size of the ceramic phase in the aluminum matrix may vary from less than 0.01 microns to about 1 micron or larger, up to about 25 microns, dependent upon a number of factors in preparation. Ceramic particles of less than 1 micron diameter have been found preferable for many purposes, and some composites in accordance with this invention have been found to have a particle size distribution in which high proportions, e.g., substantially all, of the ceramic particles appear to be less than 1 micron in size. Further, composites in which substantially all particles are smaller than 2 microns have been prepared, in which well over 50 percent of the particles are smaller than 1 micron. The factors which effect particle size include reaction heat-up rate, reaction temperature, cool-down rate, and crystallinity and particle size of starting materials. Appropriate starting material sizes may range from less than 5 microns to more than 200 microns, with one normally utilizing larger particle size powders for economic reasons.

It has been found that some specific reactant properties have a greater impact than powder particle size on the particle size of the ceramic produced. For example, the use of amorphous boron results in the precipitation of a finer grain size titanium diboride than does the use of crystalline boron of otherwise comparable nature. The precipitation of specific grain size ceramic phase may be selectively controlled by proper control of starting composition, temperature of reaction, and cool-down rate.

Example 1 illustrates the in-situ precipitation of fine particles of titanium diboride in aluminum by a powder-powder mode reaction.

Example 1

A mixture of 34 percent by weight of titanium powder, 16 percent by weight of boron and 50 percent by weight of aluminum was isostatically compacted to 38,000 pounds per square inch. The compacted artifact was then heated in a furnace set at a temperature of 800°C. Upon reaching approximately 670°C, a rapid increase in temperature to approximately 1250°C was noted. The rate of increase in temperature was very rapid (greater than 900°C per minute) followed by a fast cool down rate of approximately 400°C per minute. On subsequent examination the sample was found to contain a fine dispersion (0.1 - 3 microns) of titanium diboride particles in an aluminum matrix.

An alloy-alloy reaction, in the liquid state, is exemplified by Examples 2 and 3 described below.

15 Example 2

Two separate aluminum alloys, one containing 10 percent titanium, and the other 4 percent boron, by weight, were placed in an alumina crucible and heated to 1400°C for one hour under an argon atmosphere. Mixing of the alloys occurred through diffusion and thermal effects. The experiment was performed at 1400°C to ensure that all of the titanium and boron alloys were dissolved, thereby allowing the titanium diboride to fully precipitate, it being considerably less soluble than the individual elements. Subsequent SEM/EDS analysis of the metal matrix composite produced identified submicron TiB_2 particles dispersed in an aluminum matrix. While this experiment was intended to completely dissolve the titanium aluminide and aluminum boride such that all the titanium and boron were freely in solution in the aluminum, it was recognized that because of its limited solubility titanium diboride could precipitate at any temperature above the melting point of the solvent metal, even if not all of the alloys were dissolved.

Example 3

To support the contention that it was not necessary to fully dissolve the titanium and boron in the alloys, three experiments similar to Example 2 were performed, except that the maximum
5 temperatures achieved were limited to 1200°C, 1000°C and 800°C respectively. As in Example 2, evenly dispersed TiB₂ particles were observed in the aluminum matrix, in all cases.

The following Example 4 describes the production of aluminum/titanium diboride composites by alloy-alloy reaction, in
10 the plasma state.

Example 4

In this example, a reaction is achieved by striking an arc between two electrodes, each containing aluminum matrix metal and one reactive species, in a closed vessel. The relative positions
15 of the electrodes is adjusted to achieve the passing of the arc. The said electrodes may also be rotated as to achieve even melting. Atomizing the homogenized molten metal into powder can be achieved in air, but is preferably performed in a non-reactive atmosphere such as an inert gas or a vacuum. Alternatively, the
20 molten metal may be collected in a heated container placed below the arc to obtain an ingot.

The reaction between the ceramic constituents within the arc yields a ceramic compound which is mixed with the matrix metal. Due to the very rapid heat up and cool down rates associated with
25 this process, a very fine distribution of ceramic particles in the metallic matrix is achieved. Striking an arc in the above manner between two electrodes, one of which contains aluminum and titanium and the other aluminum and boron, results in the formation of a fine dispersion of titanium diboride in a molten
30 aluminum droplet which solidifies as it drops through the inert gas. The powder thus produced can be subsequently processed by conventional powder metallurgical techniques. In a different variant of this process, the molten metal droplets are collected

- 20 -

in a heated crucible to produce an ingot for conventional metal working operations. In yet another variant the droplets are collected on a chilled rotating drum to produce metal-ceramic flakes.

5 The following example teaches the influence of amorphous boron on the particle size of titanium diboride precipitated in an aluminum matrix.

Example 5

10 An identical mixture (but for the use of amorphous boron instead of crystalline boron) as that described in Example 1 was prepared (i.e. approximately 34% by weight of titanium, 16% by weight of boron and 50% by weight of aluminum), compacted, and heated in a furnace. At a temperature of about 620°C, a rapid exotherm was noted. Subsequent examination revealed the presence
15 of very fine 0.01 - 1.0 micron titanium diboride particles in an aluminum matrix.

The following example illustrates the preparation of a different ceramic phase in aluminum.

Example 6

20 An experiment was conducted, whereby molybdenum disilicide was precipitated in an aluminum matrix. A mixture of approximately 7.5 percent silicon, 12.5 percent molybdenum, and 80 percent aluminum powders by weight was compacted and subsequently heated in a furnace. On attainment of a temperature of
25 approximately 640°C, a sudden exotherm was noted. Subsequent X-ray and SEM analyses confirmed the presence of particulate molybdenum disilicide in an aluminum matrix.

30 Additional experiments were conducted to produce a variety of aluminum and aluminum alloy matrix composites, as set forth in Table IV which follows.

TABLE IV

Ceramic Phase (wt%)	Matrix	Reactants (wt%)	Initiation		Particle Size (um)
			Temp. °C	Maximum Temp. °C	
TiB ₂ -100	None	Ti-69, B-31	No Reaction up to 1200°		
5 TiB ₂ -95*	Al	Ti-65.6, B-29.4, Al-5.0	580	730	
TiB ₂ -90	Al	Ti-62, B-28, Al-10	580	1120	
TiB ₂ -80	Al	Ti-55.2, B-24.8, Al-20	590	1625	1-3
TiB ₂ -60	Al	Ti-41.4, B-18.6, Al-40	680	1450	1-3
TiB ₂ -50	Al	Ti-35, B-15, Al-50	780	1488	1-5
10 TiB ₂ -40	Al	Ti-27.6, B-12.4, Al-60	680	1380	
TiB ₂ -32	Al	Ti-22, B-10, Al-68	780	1200	1-5
TiB ₂ -30	Al, Mg	Ti-20, B-5, Mg-5, Al-70	N/A	N/A	0.1-5
TiB ₂ -21	Al, Zn, Mg, Cu	Ti-14.5, B-6.7, Zn-6, Mg-5, Cu-1, Al-68	N/A	N/A	0.1-5
TiB ₂ -60	Al-Mg	Ti-41.4, B-18.6, Al-Mg-40	610	1350	1-2
15 TiB ₂ -47.5	Al-Mg, Zn, Cu	Ti-33, B-14.5, Zn-3.2, Cu-0.5, Al-Mg-48.8	610	Thermocouple Failed	
TiB ₂ -28	Al-Mg, Zn, Cu	Ti-19.3, B-8.8, Zn-5.6, Cu-0.9, Al-Mg-65.4	600	905	1.0
TiB ₂ -22	Al-Mg, Zn, Cu	Ti-14.5, B-7.1, Zn-6, Cu-1, Al-Mg-71.4	N/A	N/A	0.1-2
TiB ₂ -21	Al-Mg, Zn, Cu	Ti-14.6, B-6.8, Zn-6, Cu-1, Al-Mg-71.6	680	1000	0.1
Zr ₅ Si ₃ -30	Al	Zr-18.6, Si-11.4, Al-70	570	870	

Ceramic Phase (wt%)	Matrix	Reactants (wt%)	Initiation Temp. °C	Maximum Temp. °C	Particle Size (um)
ZrB ₂ -26	Al	Zr-21, B-5, Al-74	N/A	N/A	0.5-5
ZrB ₂ -24	Al, Mg	Zr-19, B-5, Mg-7, Al-69	N/A	N/A	0.1-1.5
5 Zr ₅ Si ₃ -35	Al	Zr-23.5, Si-10.5, Al-66	570	870	
MoSi ₂ -20	Al	Mo-12.6, Si-7.4, Al-80	N/A	N/A	0.01-5
MoB ₂ -27	Al	Mo-22, B-5.4, Al-73	N/A	N/A	0.01-3
MoB ₂ -25	Al, Mg	Mo-20, B-5, Mg-7, Al-68	N/A	N/A	0.01-3
10 WC-30	Al	W-28.2, C-1.8, Al-70	640	700	0.15-1
Cr ₃ C ₂ -30	Al	Cr-24.4, C-5.6, Al-70	630	720	
VSi ₂ -60	Al	V-28.6, Si-31.4, Al-40	820	1300	
VC-60	Al	V-48.6, C-11.4, Al-40	780	860	
VB ₂ -60	Al	V-42.2, B-17.8, Al-40	700	860	0.25-1**

*Ceramic phase not formed.

**Whiskers formed also.

- 23 -

It is understood that the above description of the present invention is susceptible to considerable modification, change, and adaptation by those skilled in the art, and such modification, changes, and adaptations are intended to be considered to be within the scope of the present invention, which is set forth by the appended claims.

- 24 -

We Claim:

1. An isotropic metal matrix composite comprising discrete, finely dispersed ceramic particles in a matrix metal selected from the group consisting of aluminum and its alloys, characterized by an elongation greater than about 1 percent, and an elastic modulus greater than that of the matrix metal in the absence of said ceramic.
2. A composite as set forth in Claim 1, wherein said ceramic particles are from about 0.01 to about 25 microns in diameter.
3. A composite as set forth in Claim 1, wherein said ceramic is selected from the group consisting of borides, carbides, oxides, nitrides, silicides, aluminides, selenides, sulfides, germanides, and mixtures thereof.
4. A composite as set forth in Claim 3, wherein at least about 50 percent by weight of said ceramic particles are less than one micron in size.
5. A composite as set forth in Claim 3, wherein said ceramic is titanium diboride.
6. A composite as set forth in Claim 5, wherein said titanium diboride constitutes from about 0.5 to about 95 percent by volume of the composite.
7. A composite as set forth in Claim 6, wherein said titanium diboride constitutes from about 5 to about 25 percent by volume of the composite.
8. A composite as set forth in Claim 5, wherein said titanium diboride is precipitated in-situ in said matrix metal.

9. A composite as set forth in Claim 8, wherein said matrix metal is aluminum.
10. A metal matrix composite comprising discrete, finely dispersed particles of an in-situ precipitated inclusion selected from the group consisting of ceramics and intermetallic compounds in a matrix metal selected from the group consisting of aluminum and its alloys.
11. A composite as set forth in Claim 10, characterized by having an elastic modulus greater than that of the matrix metal, and an elongation of greater than about 3 percent.
12. A composite as set forth in Claim 11, wherein said particles constitute from about 0.5 to about 95 percent by volume of said composite.
13. A composite as set forth in Claim 11, wherein said particles constitute from about 5 to about 25 percent by volume of said composite.
14. A composite as set forth in Claim 11, wherein said particles constitute from about 25 to about 60 percent by volume of said composite.
15. A composite as set forth in Claim 11, wherein said particles constitute more than about 60 percent by volume of said composite.
16. A composite as set forth in Claim 10, wherein said particles constitute a complex ceramic phase.
17. A metal matrix composite consisting of a matrix selected from the group consisting of aluminum and aluminum alloys, and a discrete, in-situ precipitated, finely dispersed, submicron particulate ceramic phase.

- 26 -

18. A composite as set forth in Claim 17, further characterized by elongation of at least about 3 percent and Young's Modulus greater than that of the matrix metal.
19. A composite as set forth in Claim 18, wherein said ceramic phase is selected from the group consisting of borides, silicides, carbides, oxides, and nitrides.
20. A composite as set forth in Claim 19, wherein said ceramic phase constitutes from about 5 to about 25 percent by volume of said composite.
21. A composite as set forth in Claim 19, wherein said ceramic phase is titanium diboride.
22. A composite as set forth in Claim 19, wherein said matrix comprises an aluminum alloy.

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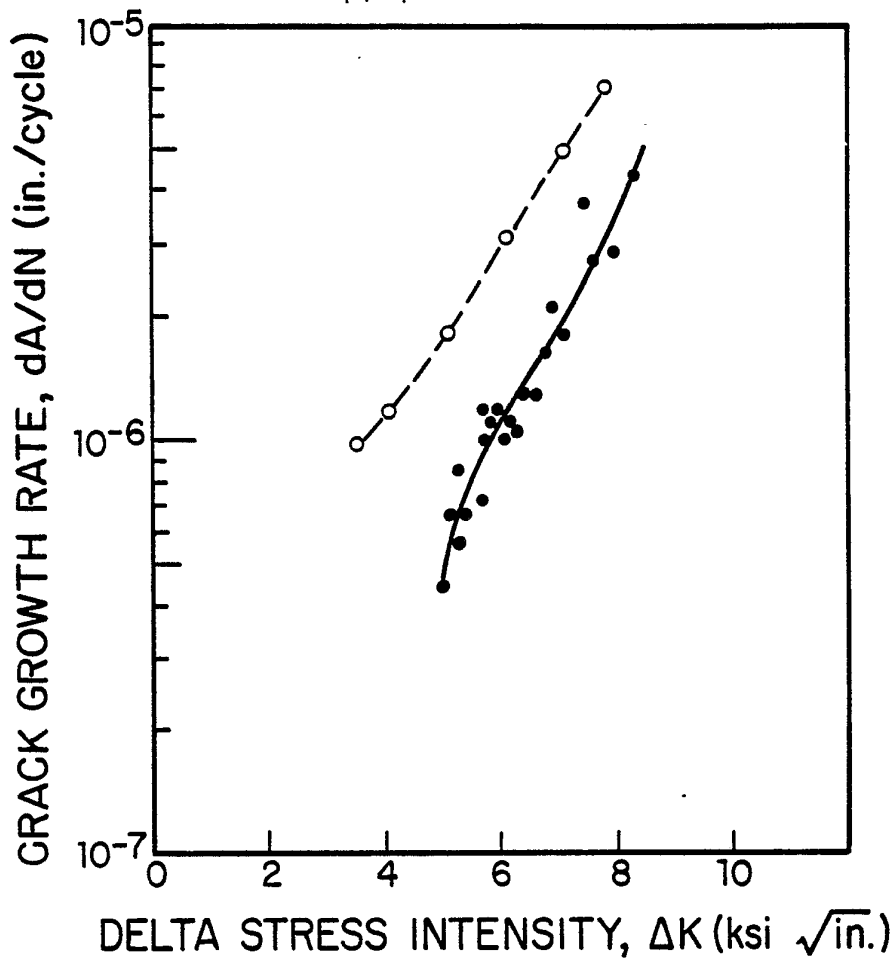


FIG. 1

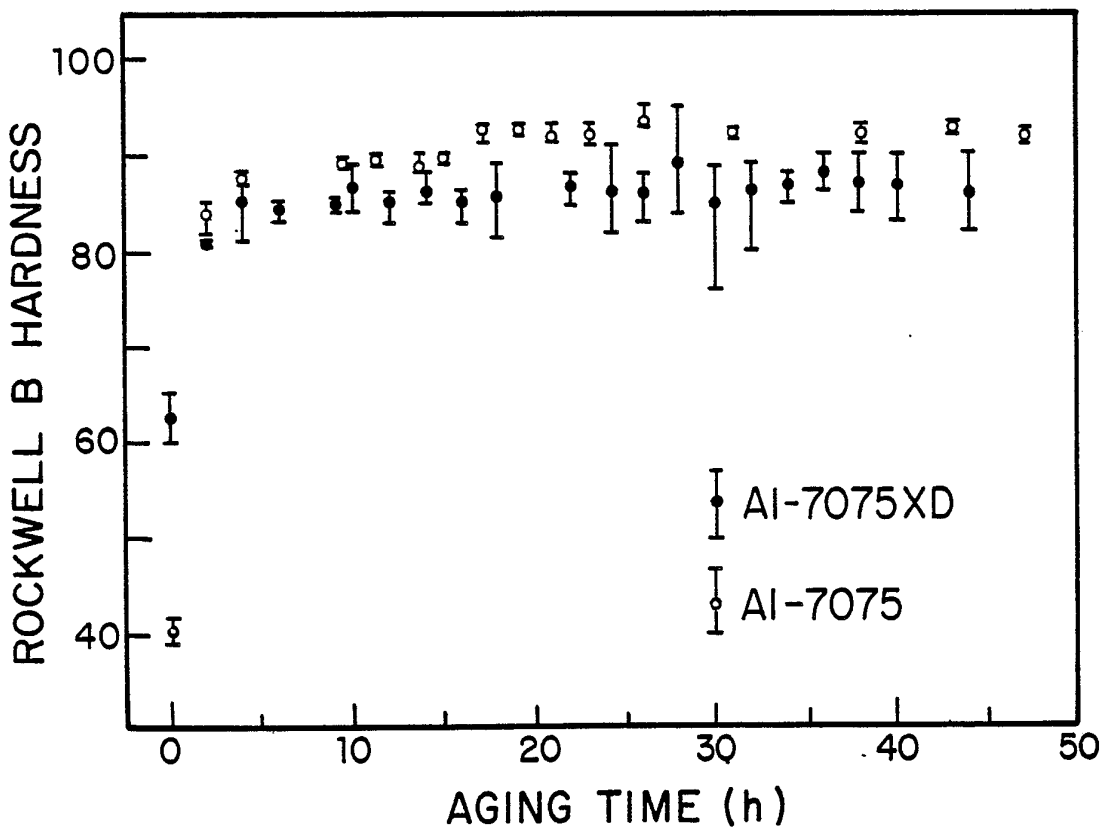



FIG. 2

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 86/00779

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		
IPC ⁴ : C 04 B 35/65; C 22 C 32/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁴	C 04 B 35/65 C 04 B 35/58 C 22 C 32/00	
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 ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	EP, A, 0117366 (ALCAN INTERNATIONAL LTD.) 5 September 1984, see claims 1,2,5,6 --	1
A	WO, A, 85/01044 (ELTECH SYSTEMS CORPORATION) 14 March 1985, see claims 1,2,4 --	1
A	FR, A, 2389584 (PPG INDUSTRIES) 1 December 1978, see claims 1-17 --	1
A	US, A, 4097567 (CEBULAK et al.) 27 June 1978, see claim 1 --	1
A	US, A, 3859399 (BAILEY et al.) 7 January 1975, see claims 1-13 --	1
A	FR, A, 2170839 (SPETSIALNOE KONSTRUKTORSKOE BJURO VAKUUMNYKH POKRYTY PRI GOSPLANE LATVIISKOI SSR) 21 September 1973, see claims 1,2 --	1
A	US, A, 3690875 (BREDZS et al.) 12 September 1972, see claims 1-8 -----	1
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"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</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"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.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the international Search	Date of Mailing of this International Search Report	
29th July 1986	22 AUG 1986	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	M. VAN MOL 	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

 INTERNATIONAL APPLICATION NO. PCT/US 86/00779 (SA 13022)

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 08/08/86

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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US-A- 4097567	27/06/78	None	
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FR-A- 2170839	21/09/73	None	
US-A- 3690875	12/09/72	DE-A,C 2005774 FR-A- 2031514 US-A- 3547673 GB-A- 1292833 US-A- 3690849	03/09/70 20/11/70 15/12/70 11/10/72 12/09/72

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