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BORON PHOSPHIDE ARTICLES AND COATINGS

Filed March 3, 1958

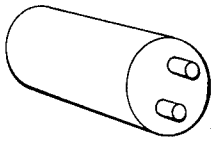


FIG. 1

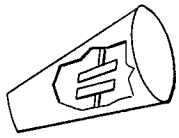


FIG. 6

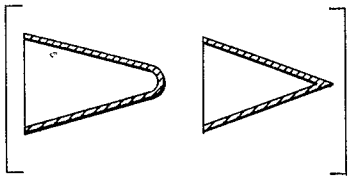


FIG. 2

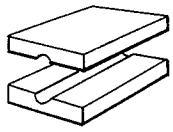


FIG. 7

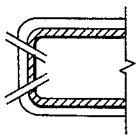


FIG. 3

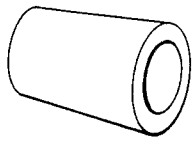


FIG. 8

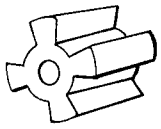


FIG. 4

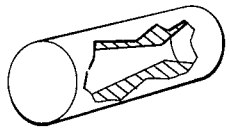


FIG. 9

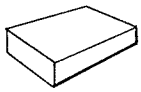


FIG. 5

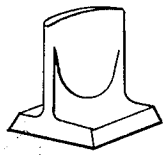


FIG. 10

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BORON PHOSPHIDE ARTICLES AND COATINGS

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The present invention relates to articles of manufacture intended for severe conditions of temperature and corrosion in the operation of guided missiles, rockets and space ships, particularly in military operations. It is an object of the invention to provide fittings and parts for such objects which must undergo great extremes of temperature, as well as severe conditions of abrasion and corrosivity.

In the operation of various types of jet and rocket engines, it is necessary that the apparatus withstand very high temperatures of the order of 4,000° F. to 10,000° F., for example, in the reaction of ethyl alkylated decaborane and fuming nitric acid as the propellants. Inasmuch as apparatus of this type is also subjected to extremely cold ambient conditions, it is obvious that the fittings of the propulsion and control systems must withstand tremendous temperature differentials. The chemicals employed as the propellants of devices of this character are also known for their corrosive action, for example, fuming nitric acid as the oxidizing agent in a number of systems. The reaction products resulting from such oxidation and decomposition reactions are known to produce corrosive reaction products, for example, nitric acid and nitrate salts from the use of hypergolic combinations exemplified by aniline and nitric acid, as well as inorganic residual materials such as fly ash and vanadium residues from kerosene. All of these materials are corrosive and erosive, so that it is necessary to make use of extremely expensive materials in order to provide satisfactory life for such fittings and parts.

It has now been found that shaped articles of manufacture, e.g., machine elements, fittings and hardware comprising crystalline boron phosphide possess unusually corrosion-resistant and wear-resistant properties, particularly at extremely high temperatures, thus solving difficult problems of the prior art in this field. Amorphous boron phosphide has been known in the past, but is an impractical construction material, since the amorphous form decomposes spontaneously when heated to temperatures above 200° C. An additional disadvantage in the use of amorphous boron phosphide is that this material is subject to spontaneous combustion in the presence of oxygen at elevated temperatures. The amorphous form of boron phosphide is obtained in carrying out the method described in J. W. Mellor's, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," vol. 8, pages 844–845 (1928). In contrast thereto the present crystalline material has a particle density of 2.94 (theoretical, 2.97) and is characterized by a cubic crystalline structure having a unit cell length of about 4.537 Angstroms.

It has now been found that boron phosphide, existing in a cubic crystalline form, is highly satisfactory either as a solid construction material or coating for jet and rocket fittings which are to be subjected to extreme conditions of temperature and corrosion.

The crystalline form of boron phosphide is resistant to oxidation when exposed for 2 minutes to an oxy-hydrogen flame giving a temperature of 4,000° F. In addition it has been found that a sample at this temperature can be subjected to an oxygen jet from a cutting torch without appreciable deterioration of the crystalline boron phosphide.

While this material is somewhat less resistant to oxidation while it is being heated up to such high temperatures, the provision of a neutral or reducing atmosphere greatly reduces any tendency towards deterioration.

Among the fittings which are contemplated in the present invention are complete vessels, and also liners for fuel tanks and other vessels. In this relationship the boron phosphide is particularly desirable, since it is not attacked by any known liquid reagent, therefore withstands the corrosive action of fuming nitric acid, aqua regia and other mineral acids, as well as basic materials, such as hydrazine.

Other elements of typical missiles, rockets, and jet planes which are readily fabricated from crystalline boron phosphide are nose cones or ogives and also tail cones. In the operation of a guided missile it is often the practice to send the missile out of the earth's atmosphere and then provide for its return into the atmosphere at a directed point. It has been found that the tremendous velocity of 3,000 to 25,000 m.p.h. during a period of 15–300 seconds with which such objects re-enter the atmosphere, results in the development of very high temperatures of the order of 10,000° F. or higher, which have in the past resulted in the burning up or destruction of conventional nose cones. However, the unique temperature stability of crystalline boron phosphide has made it possible to form nose cones of either needle-form or blunt tips which are resistant to such high temperatures and which therefore permit the re-entry of a missile or rocket into the atmosphere.

Rocket propulsion systems, whether based upon the use of liquid or solid propellants, require the production of a large volume of exit gases at a very high temperature. This is a necessary condition in order to achieve the very high speed necessary to drive such a rocket or missile. Combustion temperatures of the order of 3,000 to 5,000° F. must therefore be contained with the further requirement that corrosive reactants and reaction products may also be present as discussed above. It has been found that crystalline boron phosphide is extremely desirable as a combustion zone liner or blast tube for rockets, missiles, space ships and jet engines. An example of this type of removable combustion liner is the ram jet engine in which a hollow, tubular section serves as the combustion zone for liquid reactants which are fed into such zone, vaporized therein with a tremendous expansion in volume to the gaseous state, and discharged at a high velocity in order to propel the ram jet.

It is an advantage of the present invention that curved shapes may readily be manufactured in a form which is characterized by high strength. The production of the crystalline modification of boron phosphide results in an article of manufacture having a gross structure of the particles which provides interlocking of the crystallites. This is particularly useful in the fabrication of curved shapes since the interlocking of the crystallites results in the production of a smooth, curved surface. This effect is advantageous in the fabrication of fittings and parts which must overcome great thermal-stress and shock. Therefore, the curved shapes which are made by the present invention are desirable in providing an extremely strong coherent material which may be formed with particles of crystalline boron phosphide having substantially the theoretical density of this material.

Crystalline boron phosphide is extremely resistant to chemical attack as well as radiation so that parts may be comprised of crystalline boron phosphide in rockets, missiles and space ships which employ nuclear energy, for example, in the employment of a high intensity source of

nuclear fission or fusion which supplies energy for the operation of such missiles and other devices.

Fittings and elements of rockets and missiles comprising crystalline boron phosphide are unusually effective in withstanding the severe conditions which have been described above. For example, the nose cones are subject to the phenomenon of "ablation," i.e., the melting or burning of the nose cone together with a violent abrasion or tearing off of pieces of the cone because of the high velocity flow of the atmosphere past the cone. Nose cones of crystalline boron phosphide are more resistant than conventional materials in withstanding this great velocity.

Crystalline boron phosphide is also of utility in the fabrication of parts for sweat or transpiration cooling. This method is employed for cooling missile, rocket or space ship external and internal surfaces, such as nose cones, control surfaces, feed lines and combustion chambers which are subjected to high temperatures. The objects having a porous wall comprising crystalline boron phosphide permit the exudation of a liquid, such as water, alcohol or the liquid fuel through the porous wall so that the liquid, upon passing through the porous boron phosphide is evaporated to provide an unusually efficient cooling effect.

The above-described porous form of fabricated boron phosphide is also of utility as a filter element, particularly for corrosive liquid and gas uses. Thus, in the fuel system for a rocket or missile, it may be necessary to filter the fuel and/or oxidizing agent in order to avoid clogging the fuel lines. This presents a difficult problem in the case of corrosive agents, such as fuming nitric acid which attacks most metals. However, when a porous boron phosphide filter is inserted in the fuel or oxidant line, this filtering effect is readily accomplished without the danger of corrosion or dissolution of the crystalline boron phosphide.

The hardness of boron phosphide which corresponds to a value between 8 and 9 on Mohs' scale of hardness (diamond being 10) also makes this crystalline modification a very useful material for bearings and impellers of fuel pumps employed in rocket engine propulsion systems. In the launching of a missile or rocket it is often necessary to pump several thousands of gallons of a liquid fuel, and an oxidizing agent to the combustion zone in a period of a few minutes. Since the space and weight available for a fuel pump is very small, the fuel pump must operate under extremely difficult conditions, such as very high rotative velocities of the impeller. Large amounts of heat are therefore developed under these extreme operating conditions and it has been found that failure of conventional metallic pump impellers may readily occur. For this reason the extreme strength and corrosion resistance of crystalline boron phosphide make it desirable to employ this material in the fabrication of solid pump impellers or as a cooling material on a base of molybdenum or other refractory material. Since the high rotative speeds of the pump also result in the development of considerable heat in the bearings of the pump, it has been found desirable to employ the crystalline modification of boron phosphide as the bearing material in such heavy duty high capacity pumps for rocket propulsion systems.

The control surfaces of missiles, rockets and space ships may also be improved by constructing such fittings and hardware from the cubic crystalline form of boron phosphide. For example, the jet elevators, also called jetevators, which are used to direct a rocket by controlling the direction of the exhaust combustion gases from a rocket exhaust may be subjected to temperatures of the order of 6,000° F. It has been found that conventional metals, such as tantalum, as well as typical refractories, for example alumina and zirconia, are ineffective in this relationship because of poor thermal shock resistance and low strength when subjected to hot corrosive combustion gases, fly ash and other combustion reaction products which leave the combustion zone at high velocities of the order of hypersonic values, such as from 5 to 10 Mach numbers, e.g., above 3,000 m.p.h. Even graphite is not practical for this purpose, since this material is subject to erosion by the gas stream. Since these jet elevators and vanes must be located directly in the exhaust gas stream in order to direct and control the same for the navigation of a rocket or missile, it has been found advantageous to utilize the high thermal strength properties of boron phosphide for this purpose. The jet elevator parts may be based upon the use of solid boron phosphide in a fabricated form or may be composed of an external layer of the crystalline boron phosphide upon a base form of graphite, molybdenum, or other refractory material. Such fittings are able to withstand temperatures of several thousand degrees Fahrenheit, and therefore represent a solution to this difficult problem.

In the drawing which forms a part of the present application, certain fittings comprised of the crystalline boron phosphide in accordance with the present invention are shown in the respective figures.

FIG. 1 shows a perspective view of a fuel tank suitable for use in a rocket or missile and having an inlet and outlet line provided in one end of the cylindrical form of the said tank.

FIG. 2 illustrates nose cones suitable for use in a rocket, missile or space ship. This figure illustrates two embodiments of such nose cones, viz. the blunt and needle form nose cone, respectively.

FIG. 3 illustrates in cross-section a liner of crystalline boron phosphide as the internal element within the combustion chamber of a rocket. This combustion chamber is provided with two inlet lines for the introduction of fuels and/or oxidizing agents.

FIG. 4 shows a perspective view of a gear pump impeller made of crystalline boron phosphide.

FIG. 5 illustrates a wear plate, such as may be employed in a number of relationships for the impingement of high velocity gas streams. This element, which is made of crystalline boron phosphide, may be employed for example, as a stator in a turbine.

FIG. 6 illustrates jet elevators of crystalline boron phosphide. In this figure the two jet elevator elements are located within the exhaust tail of a rocket, missile or space ship, the said elements being provided with pivoting means in order to permit external control of the jet elevators.

FIG. 7 illustrates a pair of bearing elements of crystalline boron phosphide. These bearing parts provide for a shaft to be journalled therebetween.

FIG. 8 shows a porous tube of crystalline boron phosphide suitable for use in a sweat-cooling system.

FIG. 9 shows a cross-sectional view of a venturi throat which is intended to be used in a rocket engine. This throat must resist high temperatures and is therefore manufactured with a base form of graphite which is then coated with crystalline boron phosphide.

FIG. 10 shows a turbine blade or bucket suitable for use in a high temperature combustion engine. This bucket is formed from a prototype base of molybdenum or other refractory metal such as tungsten or tantalum and is then coated with crystalline boron phosphide.

The following examples illustrate specific embodiments of the present invention.

Example 1

A fuel tank form for a rocket, such as is shown in FIG. 1, is fabricated from stainless steel and is provided with relatively large inlet and outlet openings in one end of the cylindrical body. The stainless steel form is placed in an electrical furnace and raised to a temperature of about 1,800° F. A jet of boron trichloride is then introduced into one of the openings of the vessel, while a

jet of phosphine is introduced into another opening. The two gas streams are caused to commingle with turbulence. It is found that a chemical reaction occurs with the deposition of boron phosphide as an internal lining which covers the stainless steel to provide a corrosion-resistant layer which withstands the attack of fuming nitric acid.

Example 2

The formation of a nose cone or ogive, such as is shown in FIG. 2, is carried out by sintering a mass of pulverulent crystalline boron phosphide. A form is provided for the hot pressing of the crystalline boron phosphide to the desired shape at a temperature of about 2,700° F. It is also found that about 5% of elemental boron may also be admixed with the boron phosphide before the sintering in order to improve the bonding between the individual particles. The hot pressing operation, conducted with either of the two mixes, is found to yield a dense, smooth nose cone, which when tested with a combustion flame at 5,400° F. is found to be unaffected by the temperature or the combustion gases as well as the abrasive character of the high velocity gas stream.

Example 3

The combustion lining section of a rocket engine, such as is shown in FIG. 3, is made by first fabricating a cylindrical section from elemental boron which is made by utilizing an inner and outer graphite form of the desired diameter and filling the space between these two graphite cylinders with uncompacted elemental boron of 50 mesh particle size. The graphite forms with the boron between them are then placed in a high temperature furnace and heated to about 1,800° F. Provision is made to direct a stream of elemental phosphorus vapor into the space between the two graphite forms, thus permitting a chemical reaction to occur with the elemental boron. It is found that a transformation occurs with the development of a crystalline product which is found to be the cubic crystalline modification of boron phosphide with the substantially complete conversion of the elemental boron to boron phosphide. The product is an extremely non-porous and hard rocket engine liner which readily withstands temperatures of the order of 5,400° F. without deterioration.

Example 4

The formation of a gear pump impeller, such as is shown in FIG. 4, is carried out by making use of a molybdenum prototype form of the desired impeller. This form is suspended in an electric furnace maintained at about 1,800° F. Provision is also made for the introduction of a stream of boron trichloride (1 mole), elemental phosphorus (1 mole calculated as the mono-atomic form) and hydrogen (1½ moles). A chemical reaction is found to occur with the formation of the cubic crystalline form of boron phosphide as a coating on the molybdenum. This provides a dense and uniformly thick layer of boron phosphide which is resistant against abrasion and is stable at very high temperatures.

Example 5

The manufacture of wear plates, such as shown in FIG. 5, from crystalline boron phosphide is carried out by first forming a plate in a mold of the desired shape from 33% of powdered ferroboron and 67% powdered ferrophosphorus. This shape is then placed in a furnace and subjected to a temperature of about 2,700° F. At the completion of the transformation it is found that the boron phosphide exists in a matrix of iron so as to provide a wear-resistant surface. This is desirable in the manufacture of abrasion-resistant exhaust baffles in turbine and pump components of a rocket engine.

Example 6

The fabrication of jet elevators for a rocket, as shown in FIG. 6, is carried out by using a graphite prototype of the desired elevator form. This graphite model is placed in an electric furnace and subjected to a temperature of about 1,800° F., while being enveloped in convergent jets of boron trichloride (1 mole), phosphorus vapor (1.5 moles) and hydrogen (3 moles). It is found that a chemical reaction occurs between the boron trichloride, the phosphorus and the hydrogen with the formation of a thin, uniform layer of cubic crystalline boron phosphide on the graphite. The by-product of this reaction is hydrogen chloride in vapor form which is readily removed from the reaction zone. The crystalline boron phosphide layer is very hard and is resistant to attack by fuming nitric acid, standard nitric acid and inorganic nitrates at temperatures of from 1,000° F. to 6,000° F.

Example 7

The manufacture of a bearing of the cubic crystalline form of boron phosphide, such as is shown in FIG. 7, is carried out by first making a prototype of the desired bearing from powdered aluminum phosphide. This bearing form is placed in an electric furnace and subjected to a temperature of about 1,800° F. while being enveloped in a stream of boron chloride. A chemical reaction occurs between the two components with the evolution of aluminum chloride in the exit gases. The boron phosphide which is thus formed in the cubic crystalline modification has the shape of the desired bearing. The bearing thus produced is extremely hard and withstands wear even under conditions of high temperatures and corrosive atmospheres.

Example 8

The formation of a porous crystalline boron phosphide feed-line, such as is shown in FIG. 8, is carried out by making use of an inner and outer mold of graphite. The space between the two molds having the desired cylindrical configuration of a feed-line is then filled with loosely compacted elemental boron powder. The graphite forms with the boron are then placed in an electric furnace and brought to a temperature of about 1,700° F. A stream of phosphorus vapor is then passed into the furnace, causing the transformation of the elemental boron into the cubic crystalline form of boron phosphide. The product has minute residual voids in the fabricated piece, which has a porosity of about 30%.

The furnace is then cooled, after which the graphite molds are separated and the feed-line obtained as the desired article. This product has a porous structure which is of utility in making use of sweat or transpiration cooling, since the introduction of rocket fuel or other fluids, for example water or alcohol, to the outer wall will exude or sweat out a small amount of the fluid through the porous walls of the feed-line. This results in the evaporation of such exuded fluid with a consequent cooling effect.

Example 9

The fabrication of a venturi nozzle or combustion throat of the type shown in FIG. 9, is carried out by using a prototype made of graphite. The prototype has a cylindrical external shape with an internal passage through which the combustion gases are drawn to reach a high velocity at the narrowest point of the venturi section. A coating of crystalline boron phosphide is then deposited on the graphite prototype by utilizing the flame spraying process. This is carried out by introducing a supply of finely-divided boron phosphide powder (about 100 mesh) into the flame of an oxy hydrogen torch. This torch is directed towards the inner surface of the said nozzle, thereby heating the graphite form and at the same time depositing the finely-divided crystalline boron phosphide. In this way, a smooth, continuous surface of crystalline boron phosphide is obtained in the desired shape and with a thickness of about 0.01 inch, from the flame at a temperature of 2,000° F.

Example 10

A reinforced turbine blade or "bucket" suitable for

high temperature operation is made by first using a molybdenum base prototype of the desired bucket shape upon which the crystalline boron phosphide is to be deposited. The prototype is placed in a furnace and heated to a temperature of about 3,000° F. A jet of boron trichloride and another jet of phosphine are directed into the furnace to impinge on the heated molybdenum bucket formed. It is found that a uniform coating of crystalline boron phosphide is built up on the form, thus completely covering the molybdenum base.

The coating in this case is preferably of the order of about 0.005 inch thick and is found to be resistant to an oxy hydrogen flame in an intermittent heating test. The coating is also able to withstand erosion resulting from the fly ash which is normally encountered in a combustion gas stream.

A number of fabrication methods are available to produce the above-described manufactured products from crystalline boron phosphide. If it is desired to employ the crystalline material in powder form, one of the desirable methods is the hot pressing technique in which the powder is placed in a die of the desired form and subjected to an elevated temperature, for example from 1,000° F. to 6,000° F. for a sufficient time to consolidate the crystalline material and effect sufficient sintering to achieve the desired density. The pressure is generally about 500 to 20,000 p.s.i. A flux or bonding agent may also be employed in this relationship; suitable materials for this purpose include one or more of the metals: iron, nickel, cobalt, chromium, niobium, tantalum, titanium, zirconium, tungsten, molybdenum and hafnium; and the oxides alumina, zirconia, hafnia, silica, beryllia, titania, thoria, as well as combinations of the oxides and combinations with the said metals. Inorganic compounds having fluxing or bonding properties, such as the borates or phosphates, e.g., the alkali borates and phosphates may also be employed. Boron phosphate may also be employed as a bonding agent which forms a glassy matrix having the property of securing the crystalline particles of boron phosphide. Another additive which may be employed in the pressing operation is asbestos, since it has been found that when the composite article is later subjected to a vacuum heating or oxidizing condition, such as a combustion gas flame at about 6,000° F., the asbestos is burned out or fused, leaving the crystalline boron phosphide which is of utility in the use of sweat or transpiration cooling. This method is employed for cooling missile, rocket or space ship external and internal surfaces which are subjected to high temperatures. The porous objects having a wall of crystalline boron phosphide permit the exudation of a liquid, such as water, alcohol or the liquid fuel through the porous wall so that the liquid, upon passing through the porous boron phosphide is evaporated to provide an unusually efficient cooling effect.

The above-described porous form of fabricated boron phosphide is also of utility as a filter element, particularly for corrosive uses. Thus, in the fuel system for a rocket or missile, it is necessary to filter the fuel and/or oxidizing agent in order to avoid clogging the line. This presents a difficult problem in the case of corrosive agents, such as fuming nitric acid which attacks most metals. However, when a porous boron phosphide filter is inserted in the fuel or oxidant line, this filtering effect is readily accomplished without the danger of corrosion or dissolution of the crystalline boron phosphide.

In the hot pressing operation it may also be desirable to control phase changes of the boron phosphide by the use of specific additives. For example, transition temperature changes may be controlled by the addition of silicon carbide, zinc oxide and other crystalline materials to aid in the pressing operation.

Cold pressing or indenting of the crystalline boron phosphide is another fabrication method which may be employed, particularly with the use of a binder such as sodium silicate for the fabrication of various parts and fittings. The pressure utilized may be up to about 200,000 p.s.i. Suitable metallic additives which may be employed, together with the crystalline boron phosphide include iron, nickel, cobalt, chromium, niobium, tantalum, titanium, zirconium, tungsten, molybdenum and hafnium, while refractory and insulating oxides, such as alumina, zirconia, hafnia, silica, beryllia, titania, thoria may also be employed singly or in combination, including combinations with the said metals. The cold pressed material is subsequently treated in various ways, such as by sintering or partially oxidizing the fabricated article, in which case the boron phosphide may also undergo a number of controlled reactions. The use of partial oxidation of the cold pressed material also permits the development of porosity, such as by the employment of additives exemplified by naphthalene and other organic compounds as well as cork and asbestos, since the heating and oxidation results in the burning out or transformation of such binder constituents to a glassy or crystalline matrix, which together with the change in the said metals or oxide constituents serves to secure and bond the boron phosphide particles.

If a minor proportion of elemental boron is employed as an additive with the crystalline boron phosphide in either hot pressing or cold pressing, the fabricated part may be subjected to a phosphorization treatment in which the piece is subjected to the vapor of elemental phosphorus or another phosphorus compound, for example phosphine in order to consolidate the fabricated part with the transformation of the boron binding agent to boron phosphide.

In order to achieve a final crystalline boron phosphide product it is also feasible to employ starting materials other than crystalline boron phosphide. For example, the desired piece or fitting may be fabricated from a particulate form of elemental boron. This material is then reacted with elemental phosphorus in the vapor phase to form boron phosphide in situ. Other reactive starting materials which may be employed for a chemical transformation of the fabricated part include aluminum phosphide as the starting material. This material which may be employed in pulverulent form to make a crude prototype of the desired part is then reacted with boron trichloride at an elevated temperature to transform the shaped piece into pure crystalline boron phosphide with the evolution of aluminum chloride in vapor form as a by-product.

Other starting materials which are available to yield crystalline boron phosphide as the ultimate product include the combination of gaseous streams of boron trichloride and phosphine which react to deposit crystalline boron phosphide. In this relationship it is possible to make use of vapor phase deposition or impregnation of various shaped pieces, for example, graphite, molybdenum, tungsten, steel or ceramic base (e.g. porcelain or alumina) prototypes which are then coated or impregnated with the desired thickness or depth of boron phosphide. Another method which is available for such vapor phase deposition between gaseous boron reactants such as boron halides, hydrides and boron alkyls with elemental phosphorus and hydrogen. These three components when reacted in the gas phase at high temperatures yields crystalline boron phosphide.

If it is desired to make use of the cubic crystalline form of boron phosphide as a hardening element in a metallic base, for example iron in the production of a wear plate, the boron phosphide may be produced directly in such a metallic matrix. The base metals which may be employed in this relationship include the group of aluminum, magnesium, copper, titanium, chromium, manganese, vanadium, zirconium, molybdenum, tantalum, thorium, iron, nickel, lead, tin, antimony, bismuth and zinc. Articles of this type are useful to withstand wear and abrasion such as in the manufacture of a chute for

a sand or other minerals. Another use for such a reinforced metal is as a baffle in a steam turbine. The above-described process for the reaction of a phosphorus source, such as ferrophosphorus and a boron source such as ferroboron at elevated temperature results in the production of the desired cubic crystalline form of boron phosphide which is obtained in dispersed form in the iron matrix.

Pack diffusion is another method for applying crystalline boron phosphide to desired metallic or ceramic parts. In this method, particles of the crystalline boron phosphide are packed around the desired metallic or ceramic parts and the entire mixture subjected to a high temperature, e.g., about 1,500° F. to 6,000° F. for a suitable period of time to enable diffusion of the boron phosphide to take place into the desired parts and fittings.

If it is desired to coat or plate the crystalline boron phosphide on various substrates of metal or refractory parts, particularly when intricate sections are involved, a flame spraying technique is desirable. In this method, a high temperature flame such as a reducing oxy hydrogen flame is provided with finely-divided particles of crystalline boron phosphide so that the impingement of the flame upon the desired prototype base parts of metal or refractory coats the parts with a uniform and dense deposit of the crystalline boron phosphide.

Another method which may be applied is the deposition of a coating of crystalline boron phosphide by electrophoresis. This method is particularly suited for precision coating of complicated shapes. Metals and oxides selected from the group consisting of iron, nickel, cobalt, chromium, niobium, tantalum, titanium, zirconium, tungsten, molybdenum and hafnium; and the oxides alumina, zirconia, hafnia, silica, beryllia, titania, thoria, as well as combinations of the oxides and combinations with the said metals may also be applied in combination with the crystalline boron phosphide by the electrophoretic method. In this process an aqueous suspension of the crystalline boron phosphide and the desired metal or oxide is prepared, preferably with particle size ranges of from 1 to 10 microns. A suspending or dispersing agent, such as carboxymethylcellulose may also be present. The suspension preparation is then deposited upon the prototype of graphite, a metal or a fine screen metal form utilizing a plating voltage of the order of 6 to 100 volts direct current. A uniform coating of the boron phosphide, optionally with a metal and oxide therewith of the group set forth above is thus applied to the base prototype. The coating is subsequently air dried and is then treated by a low temperature hydrogen reduction in the case of the metallic oxides. Hydrogen reduction is not necessary with coatings of the metal powders, and the boron phosphide is unaffected by such treatment. The electrophoretic coating is next densified by peening, rolling or by isostatic pressing, the latter method being particularly convenient for small items. A final step after densification is a sintering of the coating to provide a uniform and strong coating which is resistant to chemicals and to abrasion.

A mechanical method of deposition which is available for the fabrication of external layers of crystalline boron phosphide is that of slurry deposition. In this method the finely-divided crystalline boron phosphide is dispersed in a liquid vehicle such as water, optionally with a dispersing or suspending agent such as carboxymethylcellulose. Additive materials, such as metals, for example, iron, nickel, cobalt, chromium, niobium, tantalum, titanium, zirconium, molybdenum and hafnium and finely-divided refractories, e.g., alumina, zirconia, hafnia, silica, beryllia, titania, and thoria may also be present.

The forms upon which the slurry is to be deposited are made with a porous structure, for example from metal powders which have been loosely consolidated to the desired shape or by the use of a fine mesh screen form having the shape of the desired object. Such a porous prototype is suspended in the liquid vehicle which is then subjected to high pressures of the order of 10,000 to 50,000 pounds per square inch. Provision is made for the liquid vehicle to be removed from the interior of the mold or prototype piece which may have an intricate form, or may consist of a simple flat plate as may be desired. As a result of the imposition of pressure upon the dispersion of the crystalline boron phosphide, the slurry is uniformly pressed against the prototype with the result that an interlocking crystalline structure is obtained without internal voids or bridges. When the desired thickness of crystalline boron phosphide has thus been formed, the coating may be subjected to further mechanical treatment. For example, the coating thus obtained by slurry dispersion may be densified by peening, rolling or isostatic pressing. Finally the deposited coating of crystalline boron phosphide, together with any additives is sintered to consolidate the coating to a dense form.

Another method of fabrication which is of utility in forming bodies from crystalline boron phosphide is the slip casting technique. In this method a slurry is made of the crystalline boron phosphide, together with any desired additive material, such as finely-divided refractories, e.g., alumina, zirconia, hafnia, silica, silicon carbide, beryllia, titania, and thoria. This mixture is then used in conventional ceramic slip casting techniques to obtain the desired shapes and fittings in a green form which is then fired, packed or sintered to consolidate the crystalline particles.

In general, fabricated articles having a crystalline boron phosphide coating or plating may be formed upon metallic or non-metallic bases, used as solid, mesh or reinforced forms. Examples of non-metallic materials as the substrate include quartz, silicon carbide and ceramic compositions such as porcelain and various types of glass.

The crystalline boron phosphide may also be mixed with amorphous boron phosphide in hot or cold molding. Various fluxes such as boron phosphate are also advantageously employed in molding operations.

The present patent application includes subject matter specifically claimed in copending applications Serial Nos. 718,462, filed March 3, 1958, now U.S. Patent No. 2,966,424; 718,463, filed March 3, 1958, now U.S. Patent No. 2,966,426; 718,464, filed March 3, 1958, now U.S. Patent No. 2,974,064; 718,465, filed March 3, 1958, 692,056, filed October 24, 1957, now U.S. Patent No. 2,984,577, and 691,158, filed October 21, 1957.

What is claimed is:

1. A hollow corrosion-resistant vessel having inlet and outlet openings and suitable to hold a corrosive fluid therein, the said vessel being comprised of crystalline boron phosphide.

2. A nose cone for a missile to be subjected to high temperatures, the said nose cone being substantially conical and comprised of crystalline boron phosphide.

3. A combustion zone liner for a rocket engine comprising substantially a hollow tubular body of an inert base material having a corrosion-resistant surface thereon comprised of crystalline boron phosphide.

4. An abrasion and corrosion resistant gear pump impeller suitable for use in a high temperature combustion engine and comprised of crystalline boron phosphide.

5. An abrasion and corrosion resistant wear plate of an iron matrix having dispersed therein crystalline boron phosphide and suitable for use in a high temperature combustion engine.

6. A jet elevator resistant to the attack of fuming nitric acid and suitable for use with high temperature combustion engines being comprised of crystalline boron phosphide.

7. An abrasion and corrosion resistant bearing adapted to support a rotating shaft and suitable for high temperature operation comprised of crystalline boron phosphide.

8. An abrasion and corrosion resistant venturi nozzle

suitable for use in high temperature combustion engines and comprised of crystalline boron phosphide.

9. An abrasion and corrosion resistant turbine bucket suitable for use in high temperature combustion engines and having a wear-resistant surface comprising crystalline boron phosphide.

10. An abrasion and corrosion resistant turbine bucket suitable for use in high temperature combustion engines and having a base form of a metal selected from the group consisting of molybdenum, tungsten, and tantalum, and being coated with a coating comprising cubic crystalline boron phosphide.

11. An abrasion and corrosion resistant turbine bucket suitable for use in high temperature combustion engines and having a base form of molybdenum and being coated with a coating comprising cubic crystalline boron phosphide.

12. An abrasion and corrosion resistant fuel filter suitable for use in high temperature combustion engines and being comprised of a porous body of crystalline boron phosphide.

13. An abrasion and corrosion resistant hollow, cylindrical tubular section comprised of porous crystalline boron phosphide suitable for use in high temperature combustion engines.

References Cited in the file of this patent

UNITED STATES PATENTS

2,793,103	Emeis	May 21, 1957
2,798,989	Welker	July 9, 1957
2,906,007	Bibbins	Sept. 29, 1959
2,920,006	Yntema	Jan. 5, 1960
2,966,424	Ruehrwein et al.	Dec. 27, 1960
2,966,426	Williams et al.	Dec. 27, 1960
2,974,064	Williams et al.	Mar. 7, 1961
3,009,230	Gruber	Nov. 21, 1961