Sept. 12, 1972 N. BREDZS ET AL **3,690,849**

CERMET-TYPE ALLOY

Original Filed Feb. 19, 1969 2 Sheets-Sheet 1

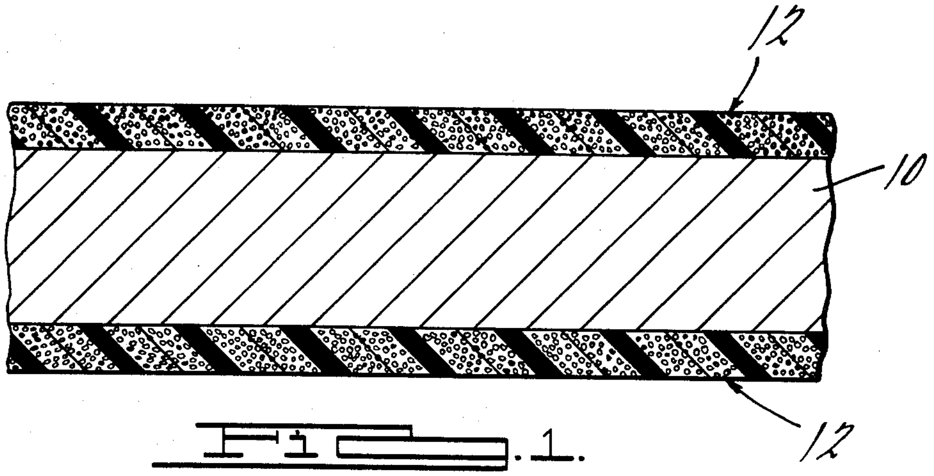

FIG. 1.

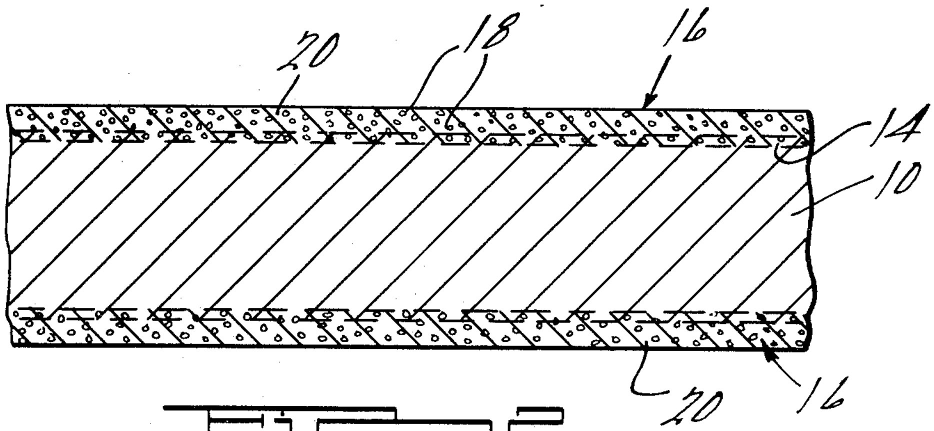

FIG. 2.

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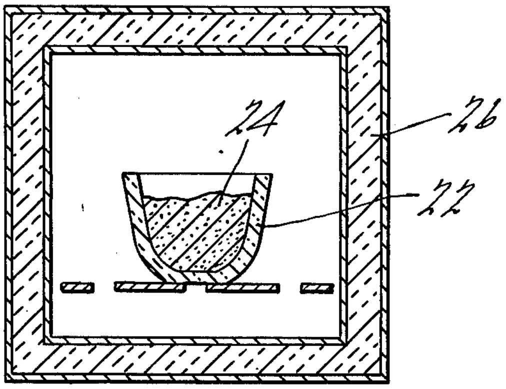

Fig. 3.

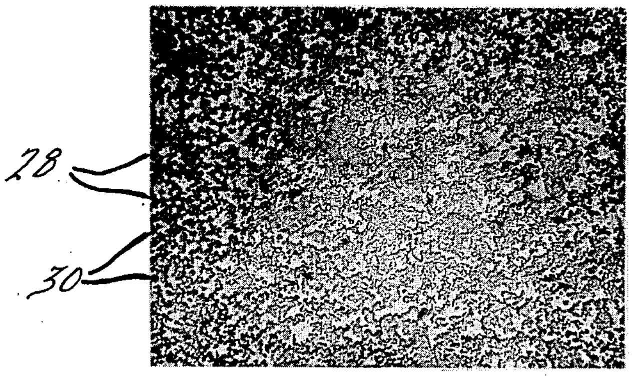

Fig. 4.

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CERMET-TYPE ALLOY

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Application Feb. 19, 1969, Ser. No. 800,540, now Patent No. 3,547,673, dated Dec. 15, 1970, which is a continuation-in-part of application Ser. No. 646,654, June 16, 1967. Divided and this application July 7, 1969, Ser. No. 871,124
Int. Cl. B22f *1/00*
U.S. Cl. 29—182.5 **3 Claims**

ABSTRACT OF THE DISCLOSURE

An improved cermet-type alloy and method of making same which is particularly adaptable for forming protective surface coatings on heat-resistant alloys. A particulated mixture is formed containing titanium and/or zirconium reactive metal constituents that undergo an exothermic reaction upon fusion at an elevated temperature in a substantially inert atmosphere with silicon and/or boron present in the mixture forming the corresponding silicides or borides of the reacted metals in situ which are subsequently precipitated as a uniformly dispersed discontinuous phase in a continuous phase of a nickel and/or cobalt base matrix. The invention also encompasses novel powder compositions for exothermically forming the cermet-type alloys and coatings.

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a divisional application of copending application Ser. No. 800,540, filed Feb. 19, 1969, for "Cermet-Type Alloy and Method of Making Same," now Pat. No. 3,547,673 which comprises a continuation-in-part application of application Ser. No. 646,654, filed June 16, 1967, for "Metallic Surface Coating and Method of Making Same," now abandoned.

BACKGROUND OF THE INVENTION

Various coating compositions and coating techniques have heretofore been used or proposed for use for providing a protective coating on metal alloys which themselves are characterized as heat and oxidation resistant alloys so as to effect a further improvement in the thermal fatigue and oxidation resistance thereof. Heat-resistant metals and alloys of the general types to which the coating composition comprising one aspect of the present invention is applicable include stainless steels, nickel-base alloys, and the so-called superalloys, such as Hastelloy-X, Inconel 600 and the like. Such heat-resistant alloys are in widespread use in the manufacture of components for gas turbine engines or the like, in which they are concurrently subjected to high stresses at elevated temperatures in the presence of an oxidizing atmosphere which effects a progressive deterioration in the physical strength properties thereof, as well as a progressive oxidation thereof. Protective coatings of the types heretofore known have either not been particularly effective in providing a substantial improvement in the corrosion resistance and thermal fatigue characteristics of such heat-resistant alloys, have been exceedingly difficult to apply, and/or have been deficient in their adherence to the substrate in order to form a continuous impervious barrier layer which is not brittle and susceptible to fracture or separation due to shock loading and stresses applied thereto.

There has also been a continuing need for improved high-strength heat-resistant metal alloys which possess improved thermal fatigue and oxidation resistance enabling such alloys to be employed directly in high temperature situations without the need of applying various protective coatings to the surfaces thereof. In accordance with another aspect of the present invention, an improved cermet-type alloy and method for making the alloy is provided which can be employed in the fabrication of components subject to high temperatures and stresses such as for components of gas turbines and the like, providing increased thermal fatigue and oxidation resistance and thereby enabling engine operation at higher temperatures, providing for a substantial improvement in operating efficiency.

SUMMARY OF THE INVENTION

In its composition aspects, the present invention is directed to an improved cermet-type alloy either in the form of an ingot or in the form of a protective coating on a substrate in which the cermet-type alloy is characterized as comprising a substantially continuous phase or matrix of a nickel and/or cobalt base alloy containing from about 10% to about 40% chromium, and preferably 15% to 25% chromium, along with other conventional impurities and alloying agents in amounts which do not appreciably reduce the heat-resistant properties of the continuous alloy matrix and a discontinuous phase of precipitated borides and/or silicides of titanium and/or zirconium which are present in the form of compressed crystals and are distributed substantially uniformly throughout the continuous matrix and are present in an amount ranging from about 2% to about 40%, and preferably from about 4% up to about 30% of the alloy.

In its method aspects, the present invention encompasses the formation of the improved cermet-type alloy by exothermically reacting a particulated mixture containing the cobalt and/or nickel-base matrix metals and a reactive metal selected from the group consisting of titanium and zirconium and a nonmetallic element selected from the group consisting of silicon and boron which are present in controlled amounts so as to effect the formation of the corresponding titanium or zirconium boride or silicide in situ through an exothermic reaction resulting from the heating of the particulated mixture at a temperature at which at least a partial fusion thereof occurs.

In the method of forming an ingot of the improved alloy, the particulated mixture is heated in a suitable refractory crucible or mold in a substantially inert atmosphere to an elevated temperature which varies depending upon the specific composition of the mixture but generally ranges from about 1900° F. up to about 2100° F. for a period of time sufficient to complete the interaction between the reactive metals and the nonmetallic elements forming a fused ingot of the cermet-type alloy.

In the method of forming protective coatings on metal substrates, the particulated mixture is applied to the surface of the metal substrate to be protected in an amount so as to provide a resultant protective layer having an average thickness of from about 0.001 to about 0.010 inch, and preferably of an average thickness of about 0.002 to about 0.005 inch. It is usually preferred to employ a suitable organic binder for preliminarily adhering the particulated mixture to the surface of the substrate, which subsequently decomposes without residue upon a heating of the coated substrate in a substantially inert atmosphere such as, for example, an argon atmosphere or in vacuum at elevated temperatures within the range hereinabove set forth, effecting at least partial fusion of the coating and an inter-reaction between the metal reactants and nonmetallic elements, effecting the formation of the cermet-type alloy coating. The heating of the coating is preferably continued so as to effect a partial diffusion of the continuous metal alloy matrix with a substrate metal, forming therewith a tenacious bond. The protective coatings thus formed, upon subsequent cooling, possess a substantially higher remelt temperature which conventionally is in the order of about 2100° F. up to about 2350° F., and above, which further enhances the effectiveness of the protective coating and provides for an improved coated article possessing increased resistance against thermal fatigue and oxidation at elevated temperatures.

A further composition aspect of the present invention is directed to a novel particulated composition containing controlled proportions of the matrix metals and reactive consituents which preferably are pre-alloyed, facilitating their handling and increasing their resistance to oxidation attack during shipment and storage, as well as providing for lower melting eutectics which reduces the temperature to which the particulated mixtures must be heated to effect a partial fusion thereof and the initiation of the exothermic reaction. The particulated compositions, when intended for use in forming protective coatings on metal substrates, are of controlled particle sizes to facilitate their application in the form of uniform coatings whereas greater latitude is provided in particle size when such particulated mixtures are employed for making ingots of the improved cermet-type alloy.

BRIEF DESCRIPTION OF THE DRAWINGS

Other advantages and benefits of the present invention will become apparent upon a reading of the following description taken in conjunction with the accompanying drawings, wherein:

FIG. 1 is a fragmentary magnified cross sectional view of a sheet of a heat-resistant alloy coated on both surfaces thereof with a particulate mixture temporarily bonded by an organic binder;

FIG. 2 is a magnified fragmentary cross sectional view similar to that shown in FIG. 1, exemplifying the protective coating after it has been fused and reacted and tenaciously bonded to the metal substrate;

FIG. 3 is a partly schematic vertical sectional view of a furnace containing a crucible in which the powder mixture is exothermically reacted forming an ingot of the cermet-type alloy; and

FIG. 4 is a photomicrograph of the metallurgical structure of the cermet-type alloy made in accordance with the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The proportions of the several constituents comprising the particulate mixture applied to a metal alloy to be protected, as well as the composition of the resultant coating formed, are described in terms of percentages by weight in the specification and subjoined claims unless expressly indicated otherwise.

In accordance with the practice of the present invention, the improved cermet-type alloy is obtained by initially forming a powder blend which contains, as its essential constituents, the matrix metal consisting of nickel and/or cobalt in addition to chromium, as well as minor proportions of other conventional impurities present in amounts which do not significantly detract from the high temperature oxidation resistance and mechanical properties of the matrix metal. The matrix metal constituent of the powder comprises about 60% to 90%, and preferably about 70% up to about 90%, of the powder and wherein the chromium constituent comprises from about 10% to 40%, and preferably from about 15% to about 25%, of the nickel and/or cobalt-chromium matrix metals. While cobalt can be substituted in whole or in part for the nickel in the matrix metal constituent, the use of nickel itself with cobalt present in amounts up to about 5% constitutes a preferred practice. In addition to the three matrix metals, namely: nickel, cobalt and chromium, the matrix metal mixture may also include additional hardening and/or strengthening agents to provide the desired physical properties of the resultant alloy formed consistent with the ultimate intended use thereof. In this regard, it is contemplated that iron can be included in the matrix metal mixture in amounts up to about 5%, manganese in amounts usually up to about 1%, as well as other conventional impurities such as aluminum, carbon, etc.

The balance of the metallic powder consists essentially of at least one reactive metal selected from the group consisting of titanium and zirconium, and at least one nonmetallic element selected from the group consisting of silicon and boron, which are effective during the fusion of the powder mixture at an elevated temperature to undergo an exothermic reaction forming the corresponding titanium or zirconium silicide or boride. In accordance with the preferred practice, the reactive metal and nonmetallic element or mixtures thereof are present in stoichiometric proportions so that no residual unreacted reaction metal and nonmetallic element is present in the resultant cermet-type alloy. It is, however, possible to incorporate quantities of titanium, zirconium and silicon in excess of the stoichiometric proportions such that the reaction metal or silicon will be present in an unreacted form in combination with the corresponding silicide in the resultant fused alloy. It is generally preferred not to employ the nonmetallic boron element in excess amounts whereby unreacted boron is present in the resultant alloy, although the reaction metals can be present in excess amounts to provide a residuary reaction metal in combination with the corresponding boride or borides in the final alloy.

The reaction product of the reaction metal and the non-metallic element occurs during the subsequent fusion of the powder blend and is exothermic, forming a nonmetallic ceramic compound or complex which is substantially insoluble in the nickel/cobalt-chromium alloy metal matrix and is present in the form of precipitated discrete discontinuous phases distributed substantially uniformly through the continuous metal alloy matrix. The proportions of the reaction metal and nonmetallic element are controlled such that the resultant alloy incorporates from about 2% to about 40%, and preferably from about 4% to about 30%, of the ceramic reaction compounds or complexes.

To achieve a resultant alloy containing the reaction compounds and/or complexes in an amount from about 2% to 40% of the cermet-type alloy, as well as the permissible inclusion of small residual unreacted portions of the zirconium, titanium and silicon constituents, the reactive portion of the powder mixture generally contains from about 1.5% to about 28% titanium or 1.8% to about 36% zirconium, and from about 0.5% to about 12% of boron or 0.5% to about 20% silicon. As previously mentioned, the specific amounts of the boron and/or silicon present in the powder mixture within the aforementioned percentage is dictated by the quantity of the titanium and/or zirconium present and preferably is controlled in stoichiometric amounts to form the corresponding silicides and borides of the reaction metal, as well as complexes thereof.

The manner by which the matrix metals and reactive constituents are introduced in the powder blend is not critical, although the nonmetallic element is usually preferably introduced in the form of a pre-alloyed powder in combination with the nickel/cobalt and chromium matrix metals. The reaction metal similarly is preferably introduced in the form of a pre-alloyed powder, preferably in proportions so as to form or approach a lower melting point eutectic of the mixture which reduces the required threshold temperature to which the powder blend must be heated to effect a partial fusion and the initiation of the exothermic reaction. In accordance with this preferred practice, a pre-alloyed powder containing 70% of the reaction metal and 30% nickel has been found particularly satisfactory, as well as pre-alloyed nickel powders containing 30% nickel and 70% titanium or, alternatively, 30% nickel and 70% zirconium. Corresponding pre-alloyed eutectic combinations of the reaction metals with cobalt include 30% cobalt and 70% titanium and 15% cobalt and 85% zirconium. The use of such pre-alloyed powders substantially simplifies the handling of the reaction metals which are generally susceptible to oxidation attack when in the pure elemental form and ordinarily require a handling thereof in a non-oxidizing atmosphere. Additionally, as previously indicated, the use of such pre-alloyed powders having compositions at or near the eutectic of the constituents provides a lower melting powder mixture enabling the initiation of the exothermic reaction at lower temperatures.

The powder mixture of the several constituents or pre-alloyed powders incorporating the reaction metals and the nonmetallic elements in an unreacted condition are usually controlled in particle size of from about 20 microns up to about 500 microns. In those instances in which the powder blend is to be employed for forming an ingot of the cermet-type alloy, greater latitude is provided in the particle size enabling use of particles having a size corresponding to maximum size as hereinabove set forth. In such instances in which the powder blend is to be employed for forming a protective coating on a metal substrate, it is generally preferred to control the particle size within a range of from about 20 microns up to about 150 microns. In the formation of protective coatings, it has generally been found that when the particle size of powder blends is greater than about 150 microns, increased difficulty is encountered in applying the powder to a substrate; whereas when particles of a size of less than about 20 microns are employed, the attainment of a satisfactory exothermic reaction is inhibited between the reaction metal and the nonmetallic element. It is for this reason that when the powder mixture is to be employed for forming a protective coating, the particle size is preferably controlled from about 20 microns up to about 150 microns. In addition, in the coating application, the particles are preferably randomly distributed over substantially the entire particle size range, thereby providing for the advantages of maximum coating density and improved quality of the resultant cermet-type coating formed.

In one method of the present invention in which a protective coating is formed on a substrate, the powdered blend is applied in the form of a uniform layer or in the form of a controlled non-uniform layer, as may be desired, to all or selected portions of the exposed surface of a substrate such as a heat-resistant alloy to be protected. The application of the powder mixture to the surface of a heat-resistant alloy can be made by any one of a variety of techniques well known in the art, and preferably by utilizing an organic binder for adhering the particles to the surface of the substrate and to retain them in proper position during the fusion operation. For this purpose, any one of a variety of organic binder materials of the types which will thermally decompose without a residue upon a heating thereof to an elevated temperature at which the coating is fused can be satisfactorily employed and include, for example, solutions of plastic materials such as polyethylene, polypropylene, polyvinyl, polyvinylidene, polyvinyl alcohol, acrylic resins, such as polymethylmethacrylate, or the like. The organic binder can be admixed with the powder blend so as to form a suitable slurry, paint or paste, and directly applied to to the part to be coated by a spray application, dipping, brushing, flooding or the like. Conventionally, it is preferred to form a spray of the organic binder, into which the dry unheated powder particles are injected, forming a composite spray which is directed against the surface of an object to be coated, forming an adherent substantially uniform film thereon, which can be readily handled as is required prior to the fusion operation. The use of such organic binder or ancillary bonding agents can be omitted when the surfaces to be coated are substantially flat and can be retained in a substantially horizontal position, maintaining uniformity of the particulated coating prior to heat fusion thereof. The specific powder blend composition of a type suitable for use in accordance with the practice of the present invention possesses a density such that coatings thereof in an amount of 125 milligrams per square inch produce a resultant fused coating of an average thickness of about 0.001 inch. Accordingly, multiples of this coating amount can be employed to produce resultant coatings having average thicknesses of from about 0.001 to about 0.010 inch thick, as may be desired.

Referring now to FIG. 1 of the drawings, a typical substrate comprising a sheet **10** of a heat-resistant alloy is illustrated having a coating **12** on each face surface thereof, comprising discrete metal particles of the powder blend retained and adhesively secured to the surfaces of the sheet by an organic binder. The coated sheet, as illustrated in FIG. 1, is subsequently treated at an elevated temperature which conventionally ranges from about 1000° F. up to about 2100° F., at which a partial fusion or melting of the metal particles occurs and during which time the organic binder thermally decomposes and volatillizes, leaving a residuary film of metal powder on the substrate. During the course of fusion of the particulated coating, the exothermic reaction occurs between the reaction metal and the nonmetallic element and concurrently a diffusion or an alloying of the resultant coating along the shaded areas indicated at **14** in FIG. 2 occurs adjacent to the surfaces of the sheet **10**, forming therewith a tenacious bond. The resultant fused coating **16** is indicated as incorporating discrete discontinuous particles of the reaction complex, indicated at 18, which are substantially uniformly dispersed throughout the continuous phase of the nickel/cobalt-chromium base matrix alloy indicated at **20**.

Various heat-resistant alloys have been coated employing the method comprising the present invention utilizing powder blends of variant compositions and have been subjected to oxidation tests and thermal fatigue tests to determine the effectiveness of the coating on the particular substrate. Conventionally, oxidation tests have been conducted by heating coated samples along with an uncoated sample as a comparative standard in an oven having an air atmosphere at a temperature of from 2100° F. to about 2200° F. The heat cycles have been conducted for 10 to 20 hour periods, at the end of which the samples are removed and are bent to determine the extent of oxidation as indicated by the brittleness of the entire sheet. Similarly, the presence of thermal fatigue is tested by passing the coated samples along with an uncoated comparative standard repeatedly through a flame, effecting a repeated heat-up and cooling thereof; after periodic cycles, the samples are investigated in the area of heat application to visually determine the presence of any surface cracks or fractures therein. The foregoing tests clearly establish the improved thermal fatigue resistance and corrosion resistance of heat-resistant alloys when protected by a selected protective coating applied in accordance with the technique comprising the present invention.

The specific benefits of the various coatings are, to some extent, governed by the specific composition of the heat-resistant alloy to which the powder blend is applied and subsequently fused and bonded. For example, the formation of a cermet-type protective coating containing, as its essential constituents, nickel, chromium, and titanium disilicide, has been found particularly satisfactory in improving the thermal fatigue resistance of Inconel, while similar coatings containing titanium diboride provide superior thermal fatigue resistance on Hastelloy X in comparison to the titanium silicide-containing coating.

On the other hand, the titanium disilicide coating possesses superior oxidation resistance to the corresponding titanium diboride coating. It will be apparent from the foregoing that the specific characteristics desired in the resultant coating, that is, thermal fatigue resistance and oxidation resistance, as well as the specific composition of the temperature-resistant alloy, will dictate the specific cermet-type coating to be used so as to maximize the benefits derived thereby.

In another method aspect of the present invention, the powder mixture incorporating the matrix metal and the reactive constituents can be employed for forming an ingot or billet of a cermet-type alloy which itself can be employed for fabricating a component satisfactory for use at elevated temperatures where high strength, oxidation resistance and thermal fatigue resistance are requisite characteristics. With reference to FIG. 3, the powder blend of the desired alloy chemistry and particle size, as hereinbefore set forth, is placed in a suitable refractory crucible or mold, indicated at **22**, and preferably is lightly compacted, such as by subjecting it to sonic or supersonic vibration, to obtain a densification of the loose free-flowing powder mixture **24**. The crucible **22** may be formed with a cavity of any desired configuration such that the resultant billet or ingot formed of the cermet-type alloy approaches a shape of the desired component to be fabricated therefrom, thereby minimizing final finishing operations. The crucible **22** is thereafter placed in a suitable furnace **26**, which is provided with a non-oxidizing protective atmosphere, and the powder mixture **24** is heated to an elevated temperature at which a partial fusion and the initiation of the exothermic reaction occurs. At the completion of the exothermic reaction, the resultant fused cermet-type alloy is removed after solidification from the crucible and is characterized as in the case of the protective coating as consisting of a substantially continuous phase of the matrix alloy having dispersed substantially uniformly therethrough a discontinuous discrete phase of precipitated compounds or complexes of the reaction metals and nonmetallic elements.

A photomicrograph, as shown in FIG. 4, is illustrative of the microstructure of a cermet-type alloy made in accordance with the practice of the present invention either in the form of a thin protective coating or in the form of an ingot. The specific micrograph shown in FIG. 4 is taken at a magnification of 120 times and reveals the alloy as having a dense, nonporous cast-type structure and comprised of a continuous phase indicated at **2B** of the matrix metals and discontinuous discrete phases comprised of crystals of the reaction constituents indicated at **30**. The specific composition of the powder blend from which the cermet-type alloy shown in FIG. 4 was produced is as follows: chromium, 17.0%; nickel, 66.5%; titanium, 7.6% and silicon, 8.9%. The inidividual discrete phases **30** of the ceramic reaction compounds and complexes, as noted in FIG. 4, are of an irregular-shaped crystalline structure formed during the precipitation of the reaction products from the molten matrix alloy. The discrete phases **30** exist in a compressed condition within the continuous phase **28**, which is a unique characteristic of the cermet-type alloy produced in accordance with the method aspects of the present invention, and is believed to contribute in part to the superior ductility, mechanical strength, oxidation resistance and thermal fatigue properties of the alloy.

In accordance with the practice of the method of forming a cermet-type protective coating or ingot as previously described, the heating of the powder blend to an elevated temperature is achieved in the presence of a non-oxidizing atmosphere to avoid oxidation attack of the powder particles as they are heated to the fusion temperature. The avoidance of significant contamination of the resultant cermet-type alloy can conveniently be achieved by employing commercially attainable vacuums or, alternatively, substantially dry inert gases, such as commercially available argon, which is used to envelop the powder blend either in the crucible or in the form of a coating on a substrate during its heating to the elevated temperature at which fusion and the exothermic reaction takes place.

The particular reaction mechanism and resultant compounds formed during the exothermic coreaction between the reaction metal and the nonmetallic element is not completely understood. It is believed, however, that the reaction occurs so as to form a compound or complex of the two constituents which is substantially insoluble in the nickel/cobalt-chromium metal alloy matrix and agglomerates to form precipitated discrete discontinuous phases dispersed substantially uniformly therethrough. In connection with powder blends containing, as their essential constituents, nickel, chromium, titanium and silicon, the proportion of the titanium and silicon present will, to some extent, determine the specific silicide formed. Thus, when a stoichiometric proportion of one gram atom of titanium is combined with one gram atom of silicon, titanium silicide (TiSi) is formed; whereas, when one gram atom of titantium is combined with two gram atoms of silicon, titanium disilicide ($TiSi_2$) is formed, Titanium trisilicide (Ti_5Si_3) is formed when the equivalent of one gram atom of titanium is reacted with 0.6 gram atom of silicon. It is believed that the resultant reaction mixture comprises combinations, as well as complexes, of these ceramic reaction products which contribute to the thermal fatigue resistance, oxidation resistance and increased solidus remelt temperature of the resultant alloy and protective coating formed.

The combination of zirconium and silicon forms zirconium silicide (ZrSi), as well as complex compounds, and the stoichiometric proportion is equivalent to one gram atom of each of these constituents. Conventionally, it has been found that the corresponding titanium silicides or complexes thereof provide improved protective coatings in comparison to those obtained employing zirconium and silicon. Similarly, the reaction product of one gram atom titanium and two gram atoms of boron form titanium boride (TiB_2), while the coreaction of one gram atom of zirconium and one gram atom of boron produces zirconium boride (ZrB). Generally, the borides of zirconium and titanium have not been found to provide an improvement in the oxidation resistance, resistance to thermal fatigue and increases in the solidus remelt temperature of the resultant coating of a magnitude equivalent to that achieved by the in situ formation of titanium silicides.

It is also contemplated within the scope of the new alloy and improved method comprising the present invention that in addition to forming the ceramic component in situ through an exothermic reaction of the reactive constituents, the in situ formed cermet can be further supplemented by the direct addition of titanium nitride (TiN) to the initial powder mixture in proportions ranging up to about 10%. The inclusion of the titanium nitride further enhances the oxidation resistance of the alloy and/or protective coating and can be incorporated in the percentages as hereinabove set forth in combination with the ceramic compounds formed in situ during the exothermic reaction further supplementing the total content of the ceramic constituent of the cermet-type alloy.

In order to further illustrate the present invention, the following examples are provided. It will be appreciated that the examples as hereinafter set forth are provided for illustrative purposes and are not intended to be limiting of the scope of this invention as set forth in the subjoined claims. In the preparation of the protective coatings as set forth in the following examples, pre-alloyed powder mixtures were employed containing the several constituents which were admixed to form a resultant particulated mixture, which was applied directly to various heat-resistant metals substrates. Two pre-alloyed powders, designated as powder A and powder B, were employed, respectively, 2.5% iron, 3.5% boron and 4.5% silicon, with powder A so as to produce a resultant coating having a nominal theoretical analysis of 75.5% nickel, 5.5% chromium, 2.2% iron, 9.7% TiB_2 and 7.1% TiS_2. The powder mixture was applied to the surface of a sheet of Inconel 600 in combination with an organic adhesive and was heated for a period of 30 minutes at 2050° F. in a dry argon atmosphere, resulting in a fine-grained thick, blue-gray colored coating. The resultant part was heated in air for several hours at 2000° F. and the coating produced a viscous, dark-green colored glass-like coating, which, upon subsequent heating at higher temperatures culminating in a temperature of 2200° F., produced a well-fused, brown-colored coating having good resistance to further oxidation.

Example VI

A powder blend was prepared comprising a mixture of powder B and the powder D in amounts of 9.5 grams and 2.0 grams, respectively, corresponding to an exact stoichiometric proportion necessary for the formation of th ecompound ZrB_2 without any excess of boron or zirconium in the resultant fused and reacted coating. The powder blend was applied to the surface of a sheet of Inconel 600 in combination with an organic binder and was heated for a period of 30 minutes at 2050° F. in a dry argon atmosphere, producing a fine-grained gray-blue coating. The resultant coating had a nominal analysis of 72.5% nickel, 12.4% chromium and 15.1% ZrB_2. The coating was observed to have a remelt temperature of 2150° F.

Example VII

A powder blend was prepared employing 36 grams of powder D and one gram of powder A, providing therewith an excess of unreacted boron. The nominal composition of the resultant fused coating was 80.1% nickel, 14.6% chromium, 2.6% boron and 2.7% TiB_2. A thin grainy, silver-gray coating was produced upon fusion of the coating for 30 minutes at 2050° F. in a dry argon atmosphere.

Example VIII

A powder blend was prepared comprising 32.88 grams of powder C and one gram of powder A, providing therewith an excess of unreacted silicon in the resultant protective coating. The nominal composition of the coating formed after fusion for 30 minutes at 2100° F. in a dry argon atmosphere was 69.7% nickel, 18.5% chromium, 7.3% silicon and 4.5% $TiSi_2$. A fine-grained, gray-brown textured coating was produced with no signs of oxidation or deterioration after heating in an air atmosphere for 150 hours at 2200° F.

Example IX

A powder blend was prepared containing 16.5 grams of powder C and one gram of powder A, producing a coating having an excess of silicon and a nominal composition of 68.6% nickel, 17.9% chromium, 4.9% silicon and 8.6% $TiSi_2$. The coating, after fusion for 30 minutes at 2100° F. in a dry argon atmosphere, had a brown-gray textured appearance and no signs of oxidation and deterioration were observed after heating in an air atmosphere for 50 hours at 2200° F.

Example X

A powder blend was prepared by mixing 24.6 grams of powder C and 10 grams of powder A to produce a resultant coating having a nominal analysis of 59.2% nickel, 13.5% chromium and 27.3% Ti_5Si_3. The coating was applied, fused and reacted in a manner as previously described. When fused in a dry argon atmosphere for a period of 30 minutes at 2150° F., a thin fine-grained blue colored coating is produced. This coating possesses remelt temperatures exceeding 2350° F.

Example XI

A powder blend is prepared by admixing powder B with a controlled proportion of powder C so as to produce a resultant protective coating having a nominal analysis of 60% nickel, 12.6% chromium and 27.4% zirconium silicide. This proportion is equal to a stoichiometric proportion of one gram atom zirconium and one gram atom of silicon to yield ZrSi.

Example XII

A powder blend is prepared comprising a mixture of powders A and C in further combination with particulated titanium nitride in an amount of 8.9% of the resultant mixture. The coating had a nominal analysis of 63.8% nickel, 16.9% chromium, 7.0% silicon, 3.4% titanium silicide and 8.9% titanium nitride. This coating possesses excellent protection against oxidation of a base metal. The application and fusion of the powdered mixture is achieved in the same manner as previously described, forming a partially diffused adherent protective coating.

Example XIII

A powder mixture is prepared comprising a mixture of powders A and C, to which 6% by weight titanium nitride is added, and a coating is formed similar to that as described in Example XII.

Example XIV

A powder blend is prepared comprising a mixture of powders A and C, to which 5% by weight of titanium nitride is added and a protective coating is formed in a manner similar to that as described in Example XII.

Example XV

Ingots having a nominal weight of about 100 grams were prepared employing the powder mixtures as described in prior Example I through XIV which were placed in a refractory crucible within a furnace provided with a substantially dry inert argon atmosphere and heated to a temperature for time periods corresponding to the temperature-time periods to which the respective coatings were subjected. In each instance, a solid ingot of the cermet-type alloy was recovered having a peripheral contour corresponding to that of the crucible and characterized by a continuous phase of the matrix metal having interspersed therein discrete phases of the ceramic compounds.

In addition to pre-alloyed powders A through D, the following additional metallic powders comprising binary alloys of cobalt and nickel with the nonmetallic elements, boron or silicon, and the reactive metals, titanium or zirconium, can also be satisfactorily employed for preparing powder blends which will exothermically react to form an alloy or coating in accordance with the practice of the present invention. The binary alloys as hereinafter set forth are selected in accordance with the preferred practice of the present invention in which the specific proportions of the ingredients form low-melting point eutectics.

POWDER E

Ingredient:	Percent by weight
Boron	4.0
Cobalt	96.0

Melting temperature: 2003° F.

POWDER F

Ingredient:	Percent by weight
Silicon	12.5
Cobalt	87.5

Melting temperature: 2183° F.

POWDER G

Ingredient:	Percent by weight
Titanium	70
Cobalt	30

Melting temperature: 1868° F.

for introducing the titanium and zirconium reaction metals into the powder mixture. The composition and characteristics of these two pre-alloyed powders are as follows:

POWDER A

Ingredient:	Percent by weight
Titanium	70
Nickel	30

POWDER B

Ingredient:	Percent by weight
Zirconium	70
Nickel	30

The remain nickel and chromium, as well as the silicon or boran constituent, are introduced employing a pre-alloyed powder designated as C and D, respectively, having nominal compositions as follows:

POWDER C

Composition

Ingredient:	Percent by weight
Carbon	0.08
Chromium	18.62
Silicon	0.75
Manganese	0.02
Iron	0.14
Sulfur	0.008
Phosphorus	0.007
Boron	0.03
Aluminum	0.01
Titanium	0.03
Zirconium	0.03
Cobalt	0.07
Nickel	Balance

Screen analysis

Mesh:	Percent
+120	Nil
−120+140	1.5
−140+200	21.6
−200+325	37.7
−325	30.0

POWDER D

Composition

Ingredient:	Percent by weight
Chromium	15.05
Boron	3.53
Carbon	0.03
Nickel	Balance

Screen analysis

Mesh:	Percent
+120	Nil
−120+150	4.1
−150+200	24.4
−200+325	34.3
−325	37.0

Variations in the specific compositions of the powder blends to be applied to a metal substrate for forming the protective coating were made by admixing controlled proportions of powder A with powder C to form the corresponding titanium silicide coating; powder A and powder D to form the corresponding titanium boride protective coating; powder B with powder C to form the corresponding zirconium silicide protective coating; and powder B with powder D to form the corresponding zirconium boride protective coating. It will be understood that while the use of pre-alloyed powders constitutes a preferred technique in accordance with the method comprising the present invention due to the convenience and simplicity provided thereby, that alternative powder mixtures also can be satisfactorily employed, including elemental powders which are admixed to as to provide similar proportions of the several constituents of the coating composition. The use of pre-alloyed powders for introducing the titanium and zirconium constituents are particularly desirable due to the reactive nature of these two reaction metals when in a pure and finely-particulated state, necessitating, in many instances, the use of inert atmospheres to avoid oxidation attack thereof.

Example I

A powder mixture was prepared comprising 41.05 grams of powder C and 5 grams of powder A, which corresponds to a stoichiometric proportion for the formation of the compound $TiSi_2$. The resultant powdered mixture was applied to the surface of a sheet of Inconel 600 employing an organic binder, and thereafter was heated for a period of 30 minutes at 2100° F. in a dry argon atmosphere to effect a fusion and exothermic reaction of the constituents thereof. The resultant protective coating formed was of a gray coarse-grained appearance and was observed to have excellent resistance to oxidation when heated in air to a temperature of 2200° F. The resultant coating had a theoretical composition of 66.5% nickel, 17.0% chromium and 16.5% titanium disilicide.

Example II

A powder blend was prepared employing a mixture of powder A and powder D utilizing 0.035 grams of powder D and one gram of powder A, which corresponds to an exact stoichiometric proportion for the formation of the compound TiB_2, without any excess of boron or titanium. The powder mixture was applied to the surface of a sheet of a type 304 stainless steel and was heated for a period of 30 minutes at a temperature of 2050° F. in a dry argon atmosphere to produce a well-fused brown colored coating. The same powder mixture was applied to the surface of a sheet of Inconel 600 under the same conditions and was observed to produce a fine-grained, blue-gray colored coating. Oxidation tests of both test panels in air when heated to temperatures up to 2100° F. did not evidence any oxidation deterioration. The resultant fused and reactive coating composition had a theoretical nominal composition of 76.37% nickel, 13.5% chromium and 10.13% titanium diboride.

Example III

A powder blend was prepared employing twice the quantity of the powder D component as used in Example II so as to provide for an excess of unreacted boron in the resulting cermet-type protective coating. The resultant fused coating had a nominal theoretical composition of 78.7% nickel, 14.2% chromium, 1.70% boron and 5.4% TiB_2. The powder blend was applied to the surface of a sheet of Inconel 600 and was heated in a dry argon atmosphere for a period of 30 minutes at 2050° F. A well-fused thin purple-gray coating was produced having a remelt temperature corresponding to the solidus of about 2150° F.

Example IV

A powder blend was prepared in which the powder A constituent was employed in an amount of twice that used in Example II in combination with powder D in order that an excess of titanium is present in the resultant protective coating. A total of 10 grams of powder D was admixed with the two grams of powder A, which, upon subsequent fusion and reaction, resulted in a protective coating having a nominal analysis of 72.8% nickel, 12.5% chromium, 5.4% titanium and 9.3% TiB_2. The coating mixture was applied in combination with an organic adhesive on the surface of an Inconel 600 sheet and was heated in a dry argon atmosphere for a period of 30 minutes at 2050° F. A well-fused silver-blue colored coating resulted.

Example V

A composite titanium boride and titanium silicide protective coating was prepared by admixing a pre-alloyed powder, similar to a composite of powders C and D, having a nominal analysis of 82.94% nickel, 6.5% chromium,

POWDER H

Ingredient:	Percent by weight
Titanium	20
Cobalt	80

Melting temperature: 2138° F.

POWDER I

Ingredient:	Percent by weight
Boron	3.8
Nickel	96.2

Melting temperature: 1976° F.

POWDER J

Ingredient:	Percent by weight
Boron	12.5
Nickel	87.5

Melting temperature: 1782° F.

POWDER K

Ingredient:	Percent by weight
Silicon	11.5
Nickel	88.5

Melting temperature: 2057° F.

POWDER L

Ingredient:	Percent by weight
Silicon	20.0
Nickel	80.0

Melting temperature: 1767° F.

POWDER M

Ingredient:	Percent by weight
Chromium	44.0
Cobalt	56.0

Melting temperature: 2552° F.

POWDER N

Ingredient:	Percent by weight
Zirconium	85.0
Cobalt	15.0

Melting temperature: 1798° F.

The following additional examples are provided to illustrate powder blends comprising mixtures of selected ones of the foregoing pre-alloyed powders which can also be satisfactorily employed in forming cermet-type alloys and coatings in accordance with the practice of the present invention.

Example XVI

A powder composition is prepared containing 100 grams of powder E, 12.65 grams powder G and 37.5 grams of powder M. This composition contains stoichiometric proportions of the titanium and boron reactive constituents to form the compound TiB_2. The resultant cermet-type alloy formed, upon fusion of the powder blend at an elevated temperature, comprises a substantially continuous matrix of the metals cobalt and chromium with the titanium diboride compound interspersed substantially uniformly therethrough as discrete phases. The composition of the resultant alloy is nominally 80.45% cobalt, 11.0% chromium and 8.55% titanium diboride.

Example XVII

A powder blend is prepared comprising a mixture of 90.35 grams of powder D and 10 grams of powder G. The proportions of the several constituents provide a continuous metal matrix consisting of nickel, chromium and cobalt and the titanium and boron reactive constituents are present in substantially stoichiometric proportions to form the compound TiB_2. The fusion of the powder blend at an elevated temperature produces a cermet-type alloy having a theoretical composition of 73.25% nickel, 13.55% chromium, 3% cobalt and 10.2% titanium diboride.

Example XVIII

A powder blend suitable for forming a cermet-type ingot or coating is prepared by mixing 100 grams of powder F, 15.22 grams of powder G and 50 grams of powder M. The proportions of the ingredients present provide for a continuous metallic matrix composed of cobalt and chromium and the reactive titanium and silicon constituents are present in substantially stoichiometric propertions to form the compound $TiSi_2$. The resulting alloy, after fusion at an elevated temperature, has a theoretical composition of 72.7% cobalt, 13.3% chromium and 14.0% titanium disilicide.

Example XIX

A powder blend is prepared to provide a resultant cermet-type alloy in which the matrix metals are nickel, cobalt and chromium by mixing 82.1 grams of powder C and 10 grams of powder G. The titanium and silicon reactive constituents are present in substantially stoichiometric proportions to form the compound $TiSi_2$. Upon exothermic reaction, the resultant cermet-type alloy in the form of an ingot or coating has a theoretical composition of 63.5% nickel, 16.6% chromium, 3.3% cobalt, 16.1% titanium disilicide, 0.2% titanium and 0.2% iron.

Example XX

A powder blend is prepared by mixing 100 grams of powder F, 19.84 grams of powder N and 50 grams of powder M, the zirconium and boron reactive constituents are present in substantially stoichiometric proportions to form the compound ZrB_2. The substantially continuous metallic matrix consists of an alloy of cobalt and chromium. The resultant cermet-type alloy produced upon fusion and reaction at an elevated temperature has a theoretical composition of 74.75% cobalt, 12.95% chromium and 12.3% zirconium diboride.

Alternative mixtures of powders A through N can be prepared in further combination with elemental powders of the several constituents to provide reactive powder mixtures and resultant cermet-type alloys having compositions within the specific proportions as hereinbefore set forth.

While it will be apparent that the description of the preferred embodiments and the specific examples disclosed are well calculated to achieve the advantages and benefits of the present invention, it will be appreciated that the invention is susceptible to modification, variation and change without departing from the spirit of the invention.

What is claimed is:

1. A cermet-type alloy consisting essentially of about 60% to about 98% of a dense, non-porous continuous metallic matrix consisting essentially of about 10% to about 40% chromium and the balance comprising at least one metal selected from the group consisting of nickel and cobalt, said continuous metallic matrix having interspersed therethrough discrete discontinuous phases consisting essentially of compounds and complexes of intermetallic reaction products selected from the group consisting of titanium silicides, titanium borides, zirconium silicides, zirconium borides, and mixtures thereof, said intermetallic reaction products formed during an in situ exothermic reaction of at least one reaction metal selected from the group consisting of titanium and zirconium and at least one nonmetallic element selected from the group consisting of silicon and boron in an inert atmosphere in the presence of metals of which said metallic matrix is comprised, said discontinuous phases comprising from about 2% to about 40% of said alloy.

2. The alloy as defined in claim **1**, wherein said continuous metallic matrix comprises about 70% to about 96% of said alloy and said discontinuous phases comprise about 4% to about 30% of said alloy.

3. The alloy as defined in claim **2**, in which said continuous metallic matrix comprises about 15% to about 25% chromium, up to about 5% cobalt, and the balance nickel.

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