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FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC
COMPOUND FORMING COMPOSITES
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3,436,248

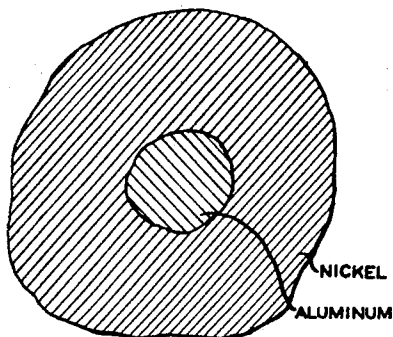


Fig. 1

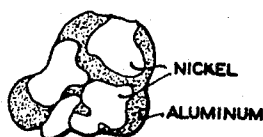


Fig. 2

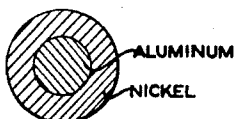


Fig. 3

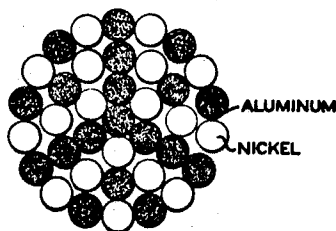


Fig. 4



Fig. 5

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FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

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Application Mar. 25, 1965, Ser. No. 442,727, now Patent No. 3,322,515, dated June 30, 1967, which is a continuation-in-part of application Ser. No. 343,705, Feb. 10, 1964. Divided and this application May 26, 1966, Ser. No. 592,238

Int. Cl. C23c 7/00, 13/02

U.S. Cl. 117—105

27 Claims

ABSTRACT OF THE DISCLOSURE

Method of coating a surface by flame spraying two or more components which will react with one another during the flame spraying to form an intermetallic compound.

This is a division of application Ser. No. 442,727, filed Mar. 25, 1965, now Patent No. 3,322,515, which was a continuation-in-part of applications, Ser. No. 72,543, filed Nov. 22, 1960, now abandoned; Ser. No. 134,544, filed Aug. 16, 1961, now Patent No. 3,254,970; Ser. No. 237,786, filed Oct. 26, 1962, now abandoned; and Ser. No. 343,705, filed Feb. 10, 1964, now abandoned.

This invention relates to the flame spraying of exothermically reacting intermetallic compound forming composites. The invention more particularly relates to the flame spraying of flame spray materials in the form of composites containing two or more components which will exothermically react with each other during the spraying, forming one or more intermetallic compounds, and to a novel group of such composites including powders and wires.

Flame spraying involves the feeding of a heat fusible material into a heating zone, wherein the same is melted or at least heat-softened, and then propelled from the heating zone in a finely divided form, generally onto a surface to be coated.

The material being sprayed is generally fed into the heating zone in the form of either a powder or a wire (the latter term designating both rods and wires). The spraying is effected in a device known as a heat-fusible material spray gun or a flame spray gun.

In the wire type flame spray gun the rod or wire of the material to be sprayed is fed into the heating zone formed by a flame of some type, where it is melted or at least heat-softened and atomized, usually by blast gas, and thence propelled in finely divided form onto the surface to be coated. The rod or wire may be a conventionally formed rod or wire of a metal, or may be formed by sintering together finely divided material, or by bonding together finely divided material by means of a plastic binder or other suitable binder which disintegrates in the heat of the heating zone, thereby releasing the material to be sprayed in finely divided form.

For spraying finely divided, i.e., powdered material, a powder type flame spray gun is used in which the powder, usually entrained in a carrier gas, is fed into the heating zone of the gun formed by a flame of some type. The powder is either melted or at least the surface of the grains heat-softened in this zone, and the thus thermally conditioned particles propelled onto a surface to provide a coating. In the powder type spray gun as no "atomizing" energy is required, a separate blast gas is often dispensed with, though the same may be supplied in order to aid in accelerating the particles and propelling them toward the surface to be coated.

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The blast gas may be provided for both the wire type and powder type guns to perform the additional function of cooling the workpiece and the coating being formed thereon.

The heat for the heating zone is most commonly produced from a flame caused by the combustion of a fuel, such as acetylene, propane, natural gas, or the like, using oxygen or air as the oxidizing agent. The heat may, however, also be produced by an electrical arc flame or, in the newer type of guns, by a plasma flame. The plasma flame may in itself constitute part of an electric arc, or, in accordance with a newer development, may be in the form of a "free plasma stream," i.e., a stream of plasma which may be considered independent of the arc as it does not contribute to the electric flow between electrodes.

Heat-fusible material spray guns utilizing electric resistance heating or induction heating as the heat source have also been proposed but have not proven commercially successful except in connection with the spraying of low melting point metals, such as solders, lead and zinc.

Flame spraying in the initial stages of its commercial development was used mostly for the spraying of various metals and was often referred to as metallizing. However, the art of flame spraying extends to the spraying of a much wider group of materials, including higher melting point or refractory metals, ceramics, cermets, and the like, and such materials are of increasing commercial interest.

In the case of spraying heat-fusible materials in the initial form of a rod or wire, the rod or wire is generally of a single composition, i.e., in the form of a specific metal, alloy, ceramic, or the like. While it is true that rods or wires formed from finely divided material bound together with a binder of plastic or the like, as mentioned above, were known, the binder generally did not take part in the spraying or contribute to the coating, and merely served the purpose of maintaining the rod or wire in shape until fed into the heating zone.

In the case of flame spray powders, while powders formed of several constituents were known, the same were generally in the form of a powder mixture of the individual constituents or, at best, a particle aggregate.

One object of this invention is the spraying of the heat-fusible material in a novel form which allows the obtaining of superior results.

A further object of this invention is a novel group of flame spray materials.

These and still further objects will become apparent from the following description read in conjunction with the drawing in which:

FIG. 1 diagrammatically shows a cross-section of a grain of novel powder in accordance with the invention;

FIG. 2 is a cross-section of a further embodiment of an aggregate grain of novel flame spray powder in accordance with the invention;

FIG. 3 is a diagrammatic cross-section of an embodiment of a novel flame spray wire in accordance with the invention;

FIG. 4 shows a cross-section of a further embodiment of a novel flame spray wire in accordance with the invention; and

FIG. 5 shows a still further embodiment of a novel flame spray wire in accordance with the invention.

In accordance with the invention, the flame spraying is effected with the heat-fusible material in the form of a composite containing at least two components which will exothermically react with each other at the temperatures developed during the spraying, forming an intermetallic compound.

The term "composite" as used herein is intended to designate a structurally integral unit and does not include a mere mixture of components which may be physically

separated without any destruction of the structure. Thus, in the case of powder, the term "composite" does not include a simple mixture of individual granules of the separate components, but requires that each of the individual granules contain the separate components which will exothermically react, forming intermetallic compounds. In the case of wire, the individual components must be incorporated in a single wire. In the composite the components must be in intimate contact with each other.

In connection with powders, each grain may consist of an aggregate containing the two components which will exothermically react, forming the intermetallic compound, but preferably the individual grains of the powder are in the form of a clad composite consisting of a nucleus of one of the components and at least one coating layer of the other component. Alternatively, the composite may consist of separate, concentric coating layers of the two components and a nucleus of still a third material.

In the case of wires, the composites may be in the form of a wire having a coating sheath of one material and a core of the other, alternate coating sheaths of the components and a core of a third material, a wire formed by twisting or rolling separate wire strands of the components, a wire consisting of a sheath of one component and a core containing the other component in powder or compacted form, a wire consisting of a sheath of one component and a core containing a compacted powder mixture of this same component material and one or more other components, a wire consisting of a plastic sheath and a core containing a compacted powder mixture of components, etc.

In order for the wires to be satisfactory for spraying, the same must not cavitate at the tip when heated, and should preferably be capable of forming a pointed or slightly tapered tip when being melted and sprayed. Thus, if the wires have an outer layer or sheath of one component and an inner core of another component, the inner core cannot have a lower melting point than the outer sheath, as otherwise the inner core will initially melt, causing cavitation at the tip. For example, if the wire is composed of nickel and aluminum as the exothermically reacting components and is in the form of a core with a coating sheath, the core must be nickel and the coating sheath aluminum, as otherwise during the spraying the core will initially melt out, causing the cavitation which will interfere with a satisfactory spraying operation. The wire having the melting-point characteristics so as to allow the melting off of the tip without this cavitation, is referred to herein and in the claims as "non-cavitating wire."

As the components, any two metallics which may be melted together to form an intermetallic compound in an exothermic reaction may be used. The components should release about 3000 calories per gram atom, and preferably at least 7500 calories per gram atom in the exothermic reaction forming the intermetallic compounds. The term "calories per gram atom" as used herein denotes the number of gram calories which the average atomic weight in grams of the intermetallic compound formed will generate in so being formed. While the components are preferably present in the stoichiometric proportions required for the formation of the intermetallic compound, it is, however, possible to also have an excess of one or the other provided the relative amounts are sufficient to release the quantities of heat indicated above in the formation of the intermetallic compounds.

An extremely large number of metal components are known which can be melted together in an exothermic reaction, forming an intermetallic compound with the generation of heat. Any of these component pairs may be utilized in accordance with the invention, it only being required that the same be capable of being initially formed into the composite suitable for spraying and that the intermetallic compounds formed therefrom liberate the required amount of heat in the intermetallic compounds-formation and are suitable as components of a sprayed

coating. As a general rule, components which will form intermetallic compounds having a higher melting point will liberate sufficient heat to be useful in accordance with the invention. In certain instances, however, components which will form intermetallic compounds which do not have as high a melting point, will also liberate sufficient heat in the exothermic reaction and thus be useful. Preferred components are aluminum with at least one of Co, Cr, Mo, W, Ta, Nb, Ti, or most preferably Ni; or silicon with at least one of Ti, Nb, Cr, W, Co, Mo, Ni or Ta.

While iron itself is not a satisfactory component, the same may be present in addition to another component, which in itself is satisfactory, such as in the form of an alloy therewith. This other component, however, must be present in amount sufficient to form the intermetallic compound with the other component of the composite, with the generation of sufficient heat to aid the spraying operation. Thus, for example, iron which just contains enough alloyed nickel to render the same rust-resistant, does not contain enough nickel for an effective exothermic reaction with aluminum. Generally an alloy of nickel and iron must contain at least about 12% nickel for this purpose.

FIG. 1 shows a composite powder consisting of a nucleus of aluminum and a coating layer of nickel. FIG. 2 shows an aggregate of these components; and FIGS. 3, 4 and 5 show various forms of wire containing these components, FIG. 3 showing a wire having an aluminum core with a nickel sheath, FIG. 4 showing a wire made of alternate strands of nickel and aluminum wire, as for example 18 strands of 25 gauge (.019" diameter) nickel wire marked 1, and 19 strands of 25 gauge aluminum wire marked 2; and FIG. 5 shows a sheath of aluminum filled with granules of nickel and aluminum.

Where one of the component metals is available as a metal hydride, the same may be used in this form rather than as a metal per se. When flame sprayed the hydrogen gas evolved from the hydride produces a reducing atmosphere, which in turn suppresses oxidation of the intermetallic compounds during and immediately after their formation. Thus, for example, in place of titanium, titanium hydride may be used as one of the components.

Also for the purpose of reducing oxidation a metal hydride, such as titanium hydride, may be added in a minor amount to the other components. Thus, for example, 1-10% by weight, and preferably 1-5% by weight, based on the total of the hydride and other components, may be used.

In addition, the powder granules and the wire may contain other conventional flame spray components, or be sprayed in admixture or in conjunction therewith. Thus, for example, the coated powders may additionally contain other coating layers of other flame spray components or may contain a nucleus of another flame spray material with alternate coating layers of the components which will exothermically react, forming the intermetallic. In a similar manner, the aggregates or the wires may contain further flame spray components, and in the case of powders, the same may additionally be admixed with any other desired flame spray powder.

The clad powders, in accordance with the invention, may be formed in any known or desired manner, and preferably by the known chemical plating processes, in which coating material is deposited on a seed or nucleus of another material, or in which multiple layers of various materials are built up on the seed material, or in which various materials are co-deposited in a single layer on the seed material.

A mode of forming the clad powders involves the depositing of a metal from a solution by reduction on a seed or nucleus, such as by the hydrogen reduction of ammoniacal solutions of nickel and ammonium sulfate on a seed powder catalyzed by the addition of anthraquinone. It is also possible to form the coating by the use of other known coating processes, such as coating by vapor de-

position, by the thermal decomposition of metal carbonyls, by hydrogen reduction of metal halide vapors, by thermal deposition of halides, hydrides, carbonyls, organo metals, or other volatile compounds, or by displacement gas plating and the like.

A preferred and greatly simplified mode of forming the clad powders in accordance with the invention is the depositing of one component as a coating in the form of a paint on the other component. Thus, one of the components which is to form the coating or cladding, may be dispersed in finely divided form in a binder or lacquer so as, in effect, to form a paint in which this component corresponds to the pigment. The paint is then used to coat core particles of the other component and the binder or lacquer allowed to set or dry. The binder material is preferably a resin which does not depend on solvent evaporation in order to form a dried or set film, and which film will decompose or break down in the heat of the spraying process. The binder, for example, may be a phenolic varnish or any other known or conventional varnish, preferably containing a resin as the varnish solids. The component which is initially mixed with the binder or varnish should preferably be as finely divided as possible, as for example —325 mesh. The other component which constitutes the core should be approximately or only slightly below the particle size ultimately desired for the spray powder. The coating of the core component with the "paint" may be effected in any known or desired manner, and it is simply necessary to mix the two materials together and allow the binder to dry or set, which will result in a fairly free-flowing powder consisting of the core component coated with a cladding of the other component bound in the binder.

The aggregates may be formed by compacting or briquetting the various components into the individual granules, or into larger aggregates and then breaking these aggregates into the granules.

The wires may be formed in the known conventional manner for forming wires with various components as, for example, by shrinking a sheath on a core, by forming the core with powder, by twisting the component wires, followed by rolling, drawing, swaging, or the like if desired.

In accordance with one mode of manufacture, one of the components may be formed into a tube or sheath and filled with a powder of the other component or a powder comprising a mixture of the two components, or containing additional components. The tube ends are then sealed and the wire reduced to the desired wire diameter by swaging, rolling or drawing. Preferably the powder or powder mixture is first compressed into cylindrical briquettes before being placed in the sheath or core. The sealing of the tube ends after loading with the powder or powder mixture can be effected, for instance, by insertion of a plug, for example of the metal of the sheath, by welding, twisting, crimping, or the like.

Powders in accordance with the invention should have the general over-all shape and size of conventional, flame-spray powders, and thus for example should have a size between —60 mesh and +3 microns and preferably —140 mesh and +10 microns (U.S. Standard screen mesh size). Most preferably the powder should be as uniform as possible in grain size, with the individual grains not varying by more than 250 microns and preferably 75 microns.

Depending on the particular flame spray process and the desired purpose, the composite powders may be sprayed per se or in combination with other different composite powders, or in combination with other conventional flame spray powders or powder components.

While the powders are preferably sprayed, as such, in a powder-type of flame spray gun, it is also possible to combine the same in the form of a wire or rod, using a plastic or similar binder, which decomposes in the heating zone of the gun, or in certain cases the powders may be compacted and/or sintered together in the form of a

rod or wire. The wires must have the conventional sizes and accuracy tolerances for flame spray wires, and thus for example may vary in size between $\frac{1}{4}$ " and 20 gauge, and are preferably of the following sizes: $\frac{3}{16}$ " $\pm .0005$ ", $-.0025$ ", $\frac{1}{8}$ " $\pm .0005$ ", $-.0025$ ", 11 gauge $\pm .0005$ ", $-.0025$ ", and 15 gauge $\pm .001$ ", with a smooth, clean finish free from surface marks, blemishes, or defects. The wires are sprayed in the conventional manner, using conventional wire-type flame spray guns.

In combining, in the exothermic reaction, forming the intermetallic compound, the components generate heat in situ in the actual material which is to form at least a part of the coating. This is to be distinguished from flame-spray processes and materials in which heat is generated by a reaction, such as an oxidation reaction, in which a foreign and non-metallic element is introduced and in which undesirable components may be produced. Aside from greatly contributing to the thermal efficiency of the process, the heat generated in situ in the formation of the intermetallic compound produces novel results, in many instances forming a denser, more adhering coating, having characteristics of at least a partially fused coating. In many instances the coating has self-bonding characteristics, so that special surface preparation, other than a good cleaning, is not required. The spraying in all other respects is effected in the conventional, well-known manner, using conventional flame spray equipment, and the conventional surface preparation may be utilized, if desired. The composites in accordance with the invention may be sprayed in conjunction with, or in addition to, other flame spray materials conventionally used in the art, or may be sprayed in combination or conjunction with the others.

The use of the composites as, for example, the nickel-aluminum composites, will generally improve the bond of the total sprayed material, and thus of the other component or components to the substrate, sometimes making the mixture self-bonding. The particle bond will be improved and the coating will be denser, so that its porosity may be decreased. In general, as little as 10% by weight of the composites in accordance with the invention will be sufficient to substantially improve the bonding characteristics and decrease the porosity of other flame spray materials, such as conventional flame spray metals, alloys or ceramics. There is, of course, no upper limit on the amount, as the composite may be sprayed per se, but generally at least about 20% by weight of the other component is required if this component is to have a pronounced effect on the characteristics of the coating.

The following examples are given by way of illustration and not limitation:

Example 1

(a) An aluminum powder having a particle size between —140 mesh and +325 mesh (U.S. Standard screen size) is coated with nickel in the known manner by the hydrogen reduction of an ammoniacal solution of nickel and ammonium sulphate, using anthraquinone as the coating catalyst. The reduction is effected at a temperature between about 300 and 350° F. in a mechanically agitated autoclave using solutions containing 40–50 grams per liter of nickel and 10–400 grams per liter of $(\text{NH}_4)_2\text{SO}_4$ and 20–30 grams per liter of NH_3 . About .2 gram per liter of anthraquinone is used as the catalyst and the autoclave is pressurized with hydrogen at a pressure of about 300 lbs. p.s.i.g. After the nickel solution is depleted and the aluminum coated with an initial coating of nickel, the solution is discharged from the autoclave and replenished with a fresh solution which need not contain further amounts of the anthraquinone coating catalyst, as the initially formed nickel coating in itself acts as a catalyst. The cycle is continuously repeated until a composite powder is formed containing about 16 to 18% by weight aluminum and 84 to 82% by weight of nickel, and a size of —100 to +270 mesh.

The powder thus formed is flame-sprayed on a mild steel plate which has been surface-cleaned with emery cloth. The spraying is effected at about 9 inches from the plate, using a powder-type flame-spray gun as described in U.S. Patent 2,961,335, issued Nov. 22, 1960 and sold by Metco Inc. of Westbury, Long Island, under the trade name of "Thermospray" powder gun. The spraying is effected at a rate of 6 to 9 lbs. of powder per hour, using acetylene gas as the fuel at a pressure of 10 p.s.i. and a flow rate of 17 to 25 cu. ft./hr. and oxygen as the oxidizing gas at a pressure of 12 p.s.i. and a flow rate of 29 to 35 cu. ft./hr.

The nickel coating and the aluminum base combine in the heat of the flame with a strong exothermic action, forming a mixture of nickel aluminum intermetallic compounds which deposit on the base as a dense, high quality coating which exhibits self-bonding characteristics. A coating layer of .002"-.004" thickness is built up in this manner. The coating may be used as a base material for spraying of further layers of different metals or the like, and serves as an excellent intermediate bonding layer.

The coating layer may also be built up to a greater thickness as, for example, .010"-.020", for use as an oxygen barrier undercoat, or to even greater thickness as, for example, .020"-.040" or thicker as a wear-resistant-oxidation-resistant surface.

Due to its self-bonding characteristics the sprayed coating will adhere to a base without the conventional surface preparation or roughening, and due to the natural characteristics of a sprayed material, will allow further materials to be sprayed thereon with good bonding. The coating formed from the powder has excellent oxidation-resistant characteristics even at high temperatures and in oxidizing atmospheres, and will for example prevent the oxidation of base materials, such as molybdenum or the like. The sprayed coatings may be used as a lining in metal-melting crucibles or molten metal-handling equipment, and will not be wetted or penetrated by many molten metals, including self-fluxing alloys. Coatings formed of the sprayed material also show good potential as high temperature, wear-resistant coatings.

When the example is repeated on a molybdenum rod of $\frac{3}{16}$ " diameter, with a coating between .010"-.012" thick, the coated rod may be repeatedly heated to approximately 2000° F. in air, in an electric furnace and cooled to room temperature with no visible oxidation occurring.

Similar results may also be obtained if the composite powder contains 10-45% by weight of aluminum and 55-90% by weight of nickel.

(b) Example 1(a) is repeated, using, however, cobalt in place of the nickel. Comparable results are obtained.

(c) Example 1(a) is repeated, using titanium hydride (TiH_2) powder in place of the aluminum and in an amount of 25-85 weight percent, and preferably 60-85 weight percent of the total. The coating formed upon spraying is hard and dense, and when sprayed on a smooth, pressed and sintered Al_2O_3 substrate, an excellent bond is formed. The spraying may be effected with an oxygen-hydrogen or oxygen-acetylene flame.

Example 2

Example 1 is repeated with the spraying being effected in turn on the following bases and prepared in the following manner:

Low alloy steels and stainless steels, smooth-ground to remove surface contamination; copper and copper base alloys, rough-ground or light-grit-blasted; aluminum and aluminum base alloys, rough-ground or light-grit-blasted; magnesium, rough-ground or light-grit-blasted; and titanium, rough-ground or light-grit-blasted.

In each case when a further material, such as steel, alumina or the like, was sprayed over the coating in the conventional and well-known manner, the same was bonded with a tenacious bond, though if this material had

been initially sprayed on the surface as prepared in the manner indicated above, a satisfactory bond would not be obtained.

Example 3

The nickel-clad powder of Example 1 is mixed with an Al_2O_3 powder having a particle size between 62 microns and 10 microns, in the ratio of about 40% of the nickel-clad powder with 60% by weight of the ceramic. The powder is sprayed, using the gun described in Example 1, on a mild steel plate which has been surface-cleaned by smooth grinding. Spraying is effected at a distance of about 9" from the plate at a rate of about 4 to 8 lbs. of powder per hr., using acetylene at a pressure of 10 lbs. p.s.i. and a flow rate of 17-25 cu. ft./hr., and oxygen at a pressure of 12 p.s.i. and a flow rate of 29-35 cu. ft./hr.

A self-bonding cermet coating is formed which showed excellent thermal shock-resistance, hardness, abrasion-resistance, and which strongly inhibited oxidation of the base.

It is possible to vary the percentages of the ceramic in the mixture between 5 and 85% in order to vary the properties of the coating. With an increased amount of the intermetallic compound in the cermet coating formed, the bonding and thermal shock-resistant properties increased, whereas with an increased amount of the ceramic, the hardness and wear-resistant properties of the coating are increased and the thermal conductivity decreased.

Example 4

Example 3 is repeated, using the following materials in place of the aluminum oxide:

Zirconia, calcium zirconate, magnesium zirconate, spinel, ceric oxide, hafnium oxide, rare earth oxides, molybdenum disilicide, tungsten silicide, chromium silicide, titanium silicide, tungsten carbide, titanium carbide and chromium carbide.

In each case an excellent coating was formed.

Example 5

A nucleus of silicon powder is coated with nickel to form a nickel-clad flame spray powder having a particle size between 100 and 325 mesh and containing 75-85% nickel based on the silicon-nickel total. The composite powder is sprayed with the flame spray gun described in Example 1 on a steel base prepared by lightly grit-blasting, using the spraying conditions as described in Example 1. During the spraying silicon combines with the nickel in an exothermic reaction, greatly enhancing the thermal efficiency of the spraying and producing an excellent coating.

Example 6

Titanium is coated with nickel as described in Example 1 to produce a powder having a particle size between 100 and 325 mesh and containing 10 to 50% nickel based on the titanium-nickel total.

The nickel protects the titanium from oxidation during storage and when spraying.

Upon spraying in the manner described in Example 1, on a base material prepared by grit blasting, the nickel and titanium combine exothermically in the flame to form a corrosion-resistant coating comprising a nickel-titanium intermetallic compound.

Example 7

Tellurium powder was coated with copper so as to form a composite having a particle size between 100 and 325 mesh and containing 50 to 80% copper based on the tellurium-copper total.

Upon spraying in the manner described in Example 1, on a base material prepared by grit-blasting, the copper and tellurium combine to form a new material.

During the spraying heat was evolved upon the combination of the copper and tellurium, increasing the thermal economy of the process.

Example 8

The nickel-clad flame spray powder of Example 1 is mixed with about 20% by weight of low pressure polyethylene powder and molded at a temperature of about 212° F. into the form of a rod of 1/8" diameter. The rod is sprayed, using a conventional wire-type flame spray gun sold by Metco Inc. of Westbury, Long Island, as the Metco-type 4-E gun. The spraying is effected with acetylene at a pressure of 15 p.s.i. and a flow rate of 37 cu. ft./hr. with oxygen as oxidizing gas at a pressure of 38 p.s.i. and a flow rate of 75 cu. ft./hr.; with air as a blast gas at a pressure of 40 p.s.i. and a flow rate of 25 cu. ft./min. The end coating produced is similar to the coating produced in Example 1.

Example 9

A wire is formed by encasing a core of nickel in a tube of aluminum and drawing to a size of .125" in diameter plus or minus .002". The wire contains 82 to 84% by weight of nickel based on the aluminum-nickel total.

The wire is sprayed, using a conventional wire type flame spray gun sold by Metco Inc. of Westbury, Long Island, as the Metco-type 4-E gun. Spraying is effected with acetylene at a pressure of 15 p.s.i. and a flow rate of 37 cu. ft./hr. with oxygen as the oxidizing gas at a pressure of 38 p.s.i. and a flow rate of 75 cu. ft./hr. Air is used as a blast gas at a pressure of 55 p.s.i. and a flow rate of 30 cu. ft./min. The end coating produced is similar to the coating produced in Example 1.

Similar results are also obtained using 55-90% by weight of nickel in the wire.

Example 10

A composite wire is formed by winding individual wires of nickel and aluminum to form a stranded wire with a diameter of .125" plus or minus .002". The wire contains 55 to 90% by weight of nickel based on the total Al-Ni. The wire is sprayed in the manner described in Example 9, with identical conditions and coating resulting.

Example 11

A silicon powder having a particle size between 140 and 325 mesh is coated with molybdenum in the known manner and a composite powder is formed containing about 35 to 39% by weight of silicon and about 61 to 65% by weight of molybdenum, and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The molybdenum coating and the silicon base combine in the heat of the flame, forming a molybdenum silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at elevated temperatures and will protect the base material from oxidation.

Example 12

A molybdenum powder having a particle size range between 140 and 325 mesh is coated with silicon in the known manner and a composite powder is formed containing about 35 to 39% by weight of silicon and about 61 to 65% by weight of molybdenum, and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting. The spraying is effected at about five inches from the plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, Long Island, New York, under the trade name of type 2MB plasma flame gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using a mixture of argon and hydrogen gas as the plasma gas, with argon at a pressure of 100 p.s.i. and a flow rate of 110 cu. ft./hr., and hydrogen at 50 p.s.i.

and a flow rate of 25 cu. ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 15 cu. ft./hr., using a standard electrode and "D" Argon nozzle, and using arc current of 400-500 amperes at 57-62 volts.

The molybdenum base and silicon coating combine in the heat of the flame, forming a molybdenum silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

Example 13

A silicon powder having a particle size between 140 and 325 mesh is coated with chromium in the known manner, and a composite powder is formed containing about 48 to 85% chromium and 15 to 52% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The chromium coating and the silicon base combine in the heat of the flame, forming a chromium-silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at elevated temperatures and will protect the base material from oxidation.

Example 14

A chromium powder having a particle size between 140 and 325 mesh is coated with silicon in the known manner, and a composite powder is formed containing about 48 to 85% chromium and 15 to 52% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting. The spraying is effected at about five inches from the plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, Long Island, New York, under the tradename of Type 2MB plasma flame gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using argon gas as the plasma gas at a pressure of 100 p.s.i. and a flow rate of 110 cu. ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 15 cu.ft./hr., using a standard electrode and "D" Argon nozzle, and using arc current of 400-500 amperes at 57-62 volts.

The chromium base and silicon coating combine in the heat of the flame, forming a chromium silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

Example 15

A zirconium powder having a particle size between 140 and 325 mesh is coated with chromium in the known manner and a composite powder is formed containing about 45% zirconium and 60% chromium by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material in the manner described in Example 1.

The chromium coating and the zirconium base combine in the heat of the flame, forming a chromium zirconium intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures.

Example 16

A titanium powder having a particle size range between 140 and 325 mesh is coated with silicon in the known manner and a composite powder is formed containing about 35 to 65% titanium and 35 to 65% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting. The spraying is effected at about five inches from the

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plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, Long Island, New York, under the trade name of Type 2MB plasma flame gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using argon gas as the plasma gas at a pressure of 100 p.s.i. and a flow rate of 110 cu. ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 15 cu. ft./hr., using a standard electrode and "D" Argon nozzle, and using arc current of 400-500 amperes at 57-62 volts.

The titanium base and silicon coating combine exothermically in the heat of the flame, forming a titanium silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

Example 17

A dysprosium powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed containing 60 to 75% dysprosium and 25 to 40% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The aluminum coating and the dysprosium base combine in the heat of the flame with a strong exothermic action, forming a dysprosium aluminum intermetallic compound which deposits on the base as a dense, high quality coating which exhibits excellent properties at high temperatures.

Example 18

A lanthanum powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed containing 70 to 75% lanthanum and 25 to 30% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by grit-blasting in the manner described in Example 1.

The aluminum coating and the lanthanum base combine exothermically in the heat of the flame with a strong exothermic action, forming a lanthanum aluminum intermetallic compound which deposits on the base as a dense, high quality coating which exhibits excellent properties at high temperatures.

Example 19

A chromium powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed consisting of 60 to 62% chromium and 38 to 40% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by grit-blasting in the manner described in Example 1.

The aluminum coating and the chromium base combine in the heat of the flame with a strong exothermic action, forming a chromium aluminum intermetallic compound which deposits on the base as a dense, high quality coating of very high melting point and excellent oxidation-resistance.

Example 20

Example 19 is repeated except that the composite powder is formed with an aluminum core and chromium coating. Identical results are obtained.

Example 21

The nickel-clad aluminum composite powder of Example 1 is mixed with cobalt bonded tungsten carbide particle powder having a particle size range of -140 mesh +10 microns, and preferably -140 +325 mesh in proportions of:

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(a) 80 weight percent tungsten carbide to 20 weight percent of the composite.

(b) 20 weight percent of the carbide to 80 weight percent of the composite, and

(c) preferably 50 weight percent each of the tungsten carbide and composite.

The powder mixtures are each flame-sprayed on a mild steel plate which has been surface-cleaned by grinding or very light sand-blast cleaning. The spraying is effected at about 8-9 inches from the plate, using a powder-type flame-spray gun as described in U.S. Patent 2,961,335 issued Nov. 22, 1960, and sold by Metco Inc. of Westbury, Long Island, New York, under the trade name of "Thermo-Spray" powder gun. The spraying is effected at a rate of 6 to 10 lbs. per hour using acetylene gas as the fuel at a pressure of 12 p.s.i. and a flow rate of 20 to 30 cu. ft./hr. and oxygen as the oxidizing gas at a pressure of 14 p.s.i. and a flow rate of 30 to 40 cu. ft./hr.

The nickel-aluminum composite powder in the mixture reacts exothermically in the flame to provide the self-bonding properties of the mixture and, being fully molten on impact with the substrate, becomes the matrix which securely binds the tungsten carbide particles together in the coating.

Used as sprayed, or finished by proper grinding procedure, the resultant coating is of a highly wear-resistant coating material, applicable to virtually any base material and not subject to the limitations of the previously used self-fluxing alloy matrix materials which must be fused at approximately 1900° F.

Example 22

Example 21 is repeated except that in place of the grade of tungsten carbide cobalt powder grains used, cobalt-bonded tungsten carbide grains with lower cobalt content and sharp, angular shape are used.

The powder was sprayed in the manner described in Example 21. The sharp, angular edges of the initial tungsten carbide particles were retained in the coating.

The deposited coating may be suitably finished by grinding for use as a wear-resistant coating or used as deposited where the coated article is to be used as a hone or lap, the sharp edges of the carbide inclusions constituting the abrading or cutting edges.

Example 23

Example 22 is repeated except that in place of the tungsten carbide grains described, cobalt-bonded tungsten carbide particles of sharp, angular shape were used which were first coated with nickel in the manner described in Example 1, so as to produce nickel-clad particles having a size between 100 and 325 mesh and containing from 20-50% nickel based on the tungsten carbide-nickel total.

Example 24

The nickel-clad aluminum composite described in Example 1 is mixed with a columbium (niobium) powder of size between -120 mesh and +10 microns and preferably -140 +325 mesh in the proportions of 60 weight percent of the nickel-aluminum composite.

The powder mixture is sprayed in the manner described in Example 21. The resultant coating is self-bonding to a wide variety of substrate materials and when properly finished, by grinding or other means, is a highly wear-resistant, hard coating.

Example 25

The nickel-clad aluminum composite described in Example 1 is mixed with a molybdenum powder of a size between -120 mesh and +10 microns and preferably -140 +325 mesh in the proportions of 65 weight percent molybdenum to 35 weight percent of the nickel-aluminum composite.

The powder mixture is sprayed in the manner described in Example 21. The resultant coating is self-bonding to a wide variety of substrate materials and when properly

finished, by grinding or other means, presents a highly wear-resistant, hard surface.

Example 26

Example 21 is repeated except in place of the tungsten carbide, other carbides such as titanium carbide, tantalum carbide, columbium carbide, chromium carbide and mixtures of the various carbides are used.

Example 27

The nickel-clad aluminum core composite from Example 21 is mixed with aluminum powder in the mesh size range -100 +325 mesh, and preferably in the -170 +325 mesh size range in the proportions of 80 weight percent nickel aluminum composite to 20 weight percent aluminum.

The mixture was sprayed in the manner described in Example 21. The coating as deposited consists of an intimate mixture of the flame-reacted nickel aluminide and aluminum securely bonded to the base and particle to particle within the coating.

Upon heat-treating in the temperature range 1250° F. to 1500° F. in reducing atmosphere, dry hydrogen for instance, the nickel aluminide and aluminum combine to form a dense, homogenous coating fused to the base material which can be used for "cathodic" protection of iron and steel subject to water and salt-water corrosion.

Example 28

The nickel-clad aluminum composite powder of Example 21 is mixed with Monel powder of a size between -100 mesh and +10 microns, and preferably between -140 and +325 mesh in the proportions 35 weight percent composite to 65 weight percent Monel.

The powder mixture was sprayed in the manner described in Example 21. The resultant coating is self-bonding to a wide variety of substrate materials and the inclusion of the nickel-aluminum composite, the components of which combine exothermically in the flame to provide the self-bonding ability of the mixture, considerably increase the particle to particle bonds within the coating and decrease the permeability of the coating.

Example 29

Example 28 is repeated except that nickel and stainless steel powders are substituted for the Monel.

Example 30

Example 28 is repeated except that chromium is substituted for the Monel.

The resultant coating when properly finished, by grinding or other means, shows high resistance to abrasion, wear, and galling by other metals, and is an excellent bearing surface.

Example 31

Finely divided aluminum powder (-325 mesh) was blended with a phenolic varnish having approximately 50% solid contents so as to form a mixture having the consistency of a heavy syrup and containing 60% by weight of the metallic aluminum.

100 grams of this varnish aluminum powder mixture was added to 240 grams of nickel powder having a size between -200 and +325 mesh, and the two were thoroughly mixed, with the mixing continued until the varnish dried, leaving a fairly free-flowing powder in which all of the nickel core particles were clad with a dry film, which consisted of aluminum particles bonded to each other and to the core material by the phenolic binder. The powder is then warmed to 250° F. to insure complete drying. There were some minor agglomerates which were screened out and hand-milled to reduce the same to a -100 mesh powder. The end powder consisted of approximately 15 weight percent aluminum and 85 weight percent nickel due to the loss of some aluminum during the milling. The powder is sprayed in the

manner described in Example 1 producing a similar coating having, however, more than twice the tensile strength of the coating produced in Example 1.

Example 32

(a) A mixture of 6 weight percent aluminum and 94 weight percent nickel powder are thoroughly blended and pressed together in the form of cylindrical briquettes which are loaded into an aluminum tube of .375" outside diameter, after which the tube ends are welded closed. The 3/8" diameter feed stock is then swaged to 1/4" diameter, then to a 3/16" diameter and then to a 1/8" finished wire diameter. The wire is then annealed and coiled. The wire is then sprayed, using the conventional wire type flame spray gun sold by Metco Inc. as the Metco Type 4-E gun. Spraying is effected, using acetylene at a pressure of about 15 lbs. p.s.i. and a flow rate of 37 cu. ft./hr. and oxygen as the oxidizing gas at a pressure of 38 lbs. p.s.i. and flow rate of 75 cu. ft./hr. Air is used as a blast gas at a pressure of 55 lbs. p.s.i. and flow rate of 30 cu. ft./min. The wire is sprayed at a rate of 5 ft. per minute. The spray material is deposited on a surface of ground and machine-finished, cold rolled steel with a tensile bond strength of 3820 lbs. p.s.i. The sprayed coating is hard and dense; it is wear- and oxidation-resistant and it also could serve as a base for further spraying.

(b) Example 32(a) is repeated except that chromium is used in place of the nickel powder in amounts of from 24-95 weight percent, based on the total of the aluminum and chromium. Spraying results in a high quality coating which has self-bonding properties and is resistant to oxidation at high temperatures.

(c) Example 32(a) is repeated, using columbium powder in place of the nickel powder in amounts of from 40-90 and preferably 50-55 weight percent, based on the total of the columbium and aluminum. The sprayed coating formed is a high quality coating which is resistant to oxidation at high temperatures and may be used to protect tantalum and molybdenum bases from oxidation.

(d) Example 32(a) is repeated, using tantalum powder in place of the nickel powder in amounts of 40-90 weight percent and preferably 65-75 weight percent of tantalum, based on the total of tantalum and aluminum. The sprayed coating is a dense, high quality coating which is self-bonding and is resistant to oxidation at high temperatures.

(e) Example 32(a) is repeated, using boron powder in place of the nickel powder in amounts of 40-90 weight percent, based on the total of boron and aluminum. The resulting sprayed coating is self-bonding and is resistant to oxidation at high temperatures.

(f) Example 32(c) is repeated except that the powder additionally contains 0.5 to 5 weight percent of boron, and/or 0.5 to 5 weight percent of silicon, based on the total of the components. The coating formed is similar to that obtained in Example 32(c) except that on heating to high temperature in air, a very thin, dense, adherent, protective oxide film forms on the surface of the inter-metallic compound formed, which is resistant to spalling due to thermal shock, and which is believed self-healing.

(g) Example 32(a) is repeated except that tungsten carbide containing 12% binder and having a particle size below -140 mesh is added in amount of 5-70 weight percent, based on the total of the components. The resulting coating is a dense, extremely wear-resistant coating, which has self-bonding properties. This example may be further repeated, using in place of the tungsten carbide specified, crystalline tungsten carbide, aluminum oxide, diamonds or any other abrasive material.

(h) Example 32(a) is repeated. However, 1-10% by weight and preferably 1-5% by weight of titanium hydride of a size below -100 mesh and preferably below -325 mesh, based on the total of the components, is added to the core material. The results are the same as indicated in Example 32(a) except that the coating formed is of im-

proved physical strength, containing considerably less oxide inclusions. In place of the titanium hydride other metal hydrides may be used.

(i) Example 32(a) is repeated except that the nickel powder is replaced with a nichrome powder consisting of a chrome alloy containing 80% nickel and 20% chromium. When sprayed the wire gives a dense, self-bounding coating which is extremely oxidation-resistant.

(j) Example 32(a) is repeated except that the nickel powder is replaced with a powder mixture consisting of 80% by weight nickel and 20% by weight chrome. When sprayed the wire gives a dense, self-bounding coating which is highly oxidation-resistant.

Example 33

Table I below gives examples of further component pairs which may be used to form the powders and/or wires in accordance with the invention.

Each of the component pairs as listed in Table I below may be formed into a composite powder or wire as described above, and when flame-sprayed will exothermically react, forming an intermetallic compound and high grade coating. Thus, the component pairs may be formed into clad powders as described in Example 31 and sprayed as described therein, or formed into a composite wire as described in Example 32 and sprayed as described therein.

TABLE I

Ag Ce	Ga Pr
Al As	Ga Sb
Al Au	Ga Te
Al B	Ga U
Al Ba	Ce Mg
Al Ca	Ce Nb
Al Ce	Ce Zr
Al Co	H V
Al Cr	Li In
Al La	In Te
Al Li	In Ru
Al Mo	K Sb
Al Nb	K Se
Al Ni	K Sn
Al Pr	K Te
Al Ti	La Pb
Al Zr	La Sb
Al Sb	La Sn
Al Se	La Te
Al Ta	La Zn
Al Te	Li Pb
Al U	Li Sb
Al V	Li Sn
Al W	Li Ti
As Cd	Li Zn
As Ga	Mg Sb
As In	Mg Sn
As Mg	Na Pb
As Zn	Na Sb
B Y	Na Se
B Co	Na Sn
B Cr	Na Te
B Hf	Na Ti
B Nb	Nb Si
B Ta	Ni Th
B Th	Pb Pr
B Ti	Pb Pu
B V	Pb Se
B W	Pb Ti
B Zr	Pd U
Ba Bi	Pr Sn
Ba Pb	Pr Ti
Ba Sb	Sb Zr
Be Co	Se Sn
Be Cr	Se Th
Be Ni	Se Ti
Be Np	Cu Te
Be Pu	Si Ti
Be U	Si U

TABLE I—Continued

Be Zr	Si V
Bi Ca	Si Zr
Bi Ce	Sn Te
Bi K	Sn U
Bi Li	Sn Zr
Bi Mg	Te Zn
Bi Na	Mo Be
Bi Se	Nb Be
Bi Te	Ta Be
Bi Th	V Be
Ca Pb	Ti Be
Ca Sn	Cr Si
Ca Ti	Cr Ti
Cd Li	Cr Zr
Cd Na	Mg Te
Ce In	Ni Te
Ce Mg	Si Th
Ce Pb	Si W
Ce Si	Co Si
Ce Sn	Mo Si
Ce Ti	Ni Si
Ce Zn	Si Ta
Ga Na	

We claim:

1. In the flame spray process in which a heat-fusible material is heated in a heating zone to at least heat-softened condition and propelled in such condition out of said zone in finely divided form onto a substrate, the improvement which comprises passing the heat-fusible material into said zone in the form of a composite comprising at least two distinct, components unalloyed together as a single alloy and in proportion and form sufficient to exothermically react with each other at the temperature developed in the heating zone, forming an intermetallic compound.
2. Improvement according to claim 1 in which said components are components which exothermically react with each other, with the release of at least 3,000 gram calories per gram atom.
3. Improvement according to claim 1 in which said components are components which exothermically react with each other, with the release of at least 7,500 gram calories per gram atom.
4. Improvement according to claim 1 in which one of said components is aluminum and the other nickel.
5. Improvement according to claim 4, in which said aluminum is present in amount of about 10 to 45% by weight, based on the total of nickel and aluminum.
6. Improvement according to claim 1 in which said components are component pairs selected from the group listed in Table I above.
7. Improvement according to claim 1 in which said composite contains at least one additional flame spray material.
8. Improvement according to claim 1 in which said composite is sprayed in conjunction with at least one further flame spray material.
9. In the flame spray process in which heat-fusible material is heated in a heating zone to at least heat-softened condition and propelled in said condition out of said zone in finely divided form onto a substrate, the improvement which comprises passing the heat-fusible material into said zones in the form of individual clad powder particles comprising a nucleus and a coating layer which will exothermically react with the nucleus at the temperature developed in the heating zone, forming an intermetallic compound.
10. Improvement according to claim 9 in which said components are components which exothermically react with each other, with the release of at least 3,000 gram calories per gram atom.
11. Improvement according to claim 9 in which said components are components which exothermically react

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with each other, with the release of at least 7,500 gram calories per gram atom.

12. Improvement according to claim 9 in which said nucleus is aluminum and said coating layer nickel.

13. Improvement according to claim 12 in which said aluminum is present in amount of about 10-45%, based on the total of nickel and aluminum.

14. Improvement according to claim 9 in which the nucleus and coating layers are selected from the members of the group consisting of the pairs listed in Table I.

15. Improvement according to claim 9 in which said coating layer consists of fine particles bound to said nucleus by a binder.

16. Improvement according to claim 9 in which said clad powder particles are in admixture with another flame spray powder.

17. In the flame spray process in which heat-fusible material is heated in a heating zone to at least heat-softened condition and propelled in said condition out of said zone in finely divided form onto a substrate, the improvement which comprises passing the heat-fusible material into said zone in the form of a composite, non-cavitating wire comprising at least two components which exothermically react with each other at the temperatures developed in the heating zone, forming an intermetallic compound.

18. Improvement according to claim 17 in which said components are components which exothermically react with each other, with the release of at least 3,000 gram calories per gram atom.

19. Improvement according to claim 17 in which said components are components which exothermically react with each other, with the release of at least 7,500 gram calories per gram atom.

20. Improvement according to claim 17 in which one of said components is aluminum and the other nickel.

21. Improvement according to claim 20 in which said aluminum is present in amount of about 10-45% by weight, based on the total of nickel and aluminum.

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22. Improvement according to claim 17 in which said components are component pairs selected from the group listed in Table I above.

23. Improvement according to claim 17 in which said wire is in the form of a sheath of one component containing a powder of the other component, said sheath being of a component having a lower melting point than the other component.

24. Improvement according to claim 23 in which said sheath is an aluminum sheath and in which said core is a compacted mixture of aluminum and nickel powder.

25. Improvement according to claim 17 in which said wire is a multi-strand wire with individual strands of said components.

26. Improvement according to claim 1 in which the heat-fusible material additionally contains a metal hydride.

27. Process according to claim 47 in which one of said components is at least partially in the form of a hydride.

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**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

Patent No. 3,436,248

April 1, 196

Ferdinand J. Dittrich et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 9, line 38, "Al-Nn" should read -- Al-Ni --. Col 13, line 56, "poyder" should read -- powder --. Column 14, line 20, "end" should read -- and --. Column 15, line 32, "Ce Mg" should read -- Ge Mg --; line 33, "Ce Nb" should read -- Ge N --; line 34, "Ce Zr" should read -- Ge Zr --. Column 18, line 24, "Mackin et al." should read -- Mackiw et al. --.

Signed and sealed this 7th day of April 1970.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, :

Commissioner of Patent