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METHOD AND COMPOSITION FOR FORMING A POROUS METALLIC COATING

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This invention relates to improved metallic coating compositions for application by spraying to metal or other surfaces and to improved methods of forming metallic surface coatings.

Spray coating of metallic compositions on metal surfaces is well known to build up such surfaces to a desired dimension, to increase their corrosion resistance, and to improve their wear and abrasion resistance. Such coatings may be applied by spraying metal in molten form upon the surface to be treated, the individual droplets of the metal congealing as they strike the surface, and fusing together to build up a relatively thick, continuous coating. The metal to be sprayed may, alternatively, be sprayed at a temperature below its melting point. In this case, the metal is first powdered, and is heated during the spraying process to a temperature slightly below its melting point at which temperature it is relatively plastic. In this case, the individual particles of the sprayed metal do not weld together to form a continuous coating, but being plastic, deform when they impinge upon the surface and interlock with each other, and with irregularities in the surface to form a mechanically bonded coating. Such coatings are relatively porous and are advantageous for many uses, particularly since they are capable of retaining relatively large quantities of lubricants.

The present invention pertains especially to improved compositions particularly adapted for application by the latter described method. The compositions of the invention are especially advantageous for surface coating of metallic and other surfaces to improve their wear and corrosion resistance, their capacity to retain lubricants, and to build them up dimensionally.

Accordingly, one important object of the present invention is to provide improved compositions for metal spraying.

Another object is to provide improved metal spraying compositions which when applied by spraying at temperatures below their melting temperatures produce surface coatings which are readily machinable and highly resistant to abrasion, corrosion and wear.

Another object is to provide improved metal spraying compositions for producing relatively porous, highly wear and corrosion resistant and yet readily machinable coatings.

Still another object is to provide improved methods of forming porous, metallic surface coatings.

These and other objects are accomplished according to the present invention, the improved compositions of which comprise mixtures of chromium-nickel-boron alloys with relatively soft metals such as iron, cobalt and nickel, and alloys based upon iron, nickel and cobalt. The mixtures of the invention are made up in the solid state, and are not melted together. The chromium-nickel-boron alloy in powdered form is mixed with the softer metal, which is also in powdered form. According to the invention, this mixture of powders is sprayed upon a surface to be treated at a temperature at which at least

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one of the ingredients is plastic, but below the temperature at which either of the ingredients melts. The surface coating resulting from such spraying is relatively porous and is capable of retaining relatively large quantities of a lubricant. The chromium-nickel-boron alloy lends hardness to the coating and provides wear and abrasion resistance closely approximating the wear and abrasion resistance achieved by a similarly sprayed coating of the chromium-nickel-boron alloy alone. The soft metal improves the machining and grinding characteristics of the coating without significantly decreasing its wear resistance in metal to metal applications. Moreover, since the softer metals are relatively inexpensive compared to the chromium-nickel-boron alloy, the compositions of the invention provide metallic surface coatings of high quality at reduced cost.

It should also be noted that the hard chromium-nickel-boron alloys are non-heat treatable, and will retain their hardness despite repeated heating up to their melting temperatures and cooling in any manner.

The chromium-nickel-boron alloys that are preferred for use in the practice of the invention are those falling within the following analyses:

	Percent
25 Carbon-----	0.30 to 1.00
Chromium-----	8.00 to 18.00
Nickel-----	65.00 to 85.00
Boron-----	2.00 to 4.50
Iron-----	1.25 to 5.50
30 Silicon-----	1.25 to 5.50
Cobalt-----	Up to 1.50

These alloys are relatively hard, and are difficult to finish by machining or grinding. They can be machined only with great difficulty, using metallic carbide and aluminum oxide cutting tools. Even grinding is a relatively difficult and slow procedure when dealing with these alloys. Previously, these alloys have been widely used in a process called spray welding in which the powdered alloy is sprayed in plastic condition upon a surface to be coated, and subsequently fused on the surface by heating to a temperature above its melting temperature. Spray welding is advantageous in many instances, particularly where it is desired to achieve a non-porous surface coating of relatively great hardness. These alloys may also be sprayed in plastic form upon a surface to produce a porous coating in like manner to the spraying of the compositions according to the invention. Such porous coatings comprising only the chromium-nickel-boron alloys, however, are relatively hard and difficult to finish. They are also relatively expensive.

According to the present invention, these two disadvantages are overcome by the admixture of a relatively soft metal to the chromium-nickel-boron alloy. The soft metal may be added to the hard alloy in proportions of about 20% to 70% by weight based on the total weight of the mixture. The identity of the soft metal is not generally critical in the practice of the invention, but may be determined by the specific properties desired in the coating. For example, if a high degree of corrosion resistance is desired, the relatively soft metal should be itself corrosion resistant and may be, for example, stainless steel, or an alloy high in nickel or cobalt. If ready machinability is of importance in the coating, a readily machinable soft metal should be selected such as, for example, a soft steel.

Certain metals which are readily oxidizable or which form refractory oxides such as aluminum, magnesium, titanium, tungsten, and chromium cannot be readily sprayed under normal conditions. They may be used in the practice of the invention, however, if the proper process conditions are provided, principally with respect to

controlling the atmosphere surrounding the metals during spraying. In general, for most commercial applications it is believed that iron, cobalt, and nickel, and relatively soft alloys including iron, cobalt, or nickel as their principal ingredient will be found most advantageous for admixture with the chromium-nickel-boron alloys according to the invention.

According to a preferred embodiment of the invention, a chromium-nickel-boron alloy of the following composition is prepared:

	Percent
Carbon.....	0.50 to 1.00
Chromium.....	12.00 to 18.00
Nickel.....	65.00 to 75.00
Boron.....	2.50 to 4.50
Iron.....	3.50 to 5.50
Silicon.....	3.50 to 5.50
Cobalt.....	1.00 maximum.

This alloy may be prepared in a conventional manner. It is pulverized by any convenient means, preferably by crushing, for a sufficient time to reduce it to a relatively fine powder. The size of the individual powder particles is not critical in the practice of the invention, but will be determined principally by the type of apparatus used in the spraying process. For most commercially available apparatus adapted to spray hot metal powders, a particle size distribution of 100% through an 80 mesh screen, 99% through a 120 mesh screen, and less than 45% through a 325 mesh screen gives satisfactory results. The lower limit of size insures good flow characteristics of the powder and minimizes its tendency to compact and clog.

Although any convenient method of pulverizing may be used to prepare the metals for spraying according to the invention, crushing in a mill is preferred since it tends to produce angular particles which more readily absorb heat than spheroidal particles and are more readily locked in place by a mechanical gripping action. Particles formed by atomization of the molten metal with a gas such as steam or air tend to be relatively rounded, or spheroidal in shape. Such particles are relatively difficult to hold in a mechanically bonded coating, and also are relatively difficult to heat since their surface area is relatively small.

A quantity of 18-8 stainless steel is also pulverized to substantially the same particle size as the chromium-nickel-boron alloy. Approximately equal proportions by weight of the chromium-nickel-boron alloy and stainless steel are physically mixed together by any desired means to produce an homogeneous, uniform mixture. This mixture is then propelled, preferably by means of a carrier gas such as air through a heating medium such as an oxy-acetylene flame, and directed upon a surface to be coated. The surface to be coated is preferably prepared by chilled iron grit blasting to roughen it, so that the sprayed metal powders may interlock with the surface irregularities and bond thereto by mechanical gripping.

The heating medium may be, for example, an oxy-acetylene torch operated with a so-called "neutral" flame. Its temperature is adjusted and its distance from the surface to be coated is arranged so that at the time the metal particles of the powder strike the surface they are heated to about 1850° F. At this temperature the particles of the chromium-nickel-boron alloy are plastic and are able to deform and to interlock with the other metal particles and with the surface irregularities. Satisfactory spraying conditions may be achieved using a torch having an 8-hole tip, each hole being $\frac{1}{16}$ inch in diameter, with oxygen supplied at about 20 p. s. i., acetylene at about 12 to 15 p. s. i., and the torch being supported about $5\frac{1}{2}$ to 6 inches from the surface being coated. The powder mixture is preferably directed into the flame near the tip of the torch, and is carried to the surface by the burning gas mixture of the flame and a propellant gas stream. The propellant gas stream may be of air, and may be formed by directing air at a pressure of about 35 to 40 p. s. i. through a set of auxiliary holes, eight in number

and $\frac{1}{16}$ inch square, annularly arranged around the flame holes of the torch. Under these conditions, the powder mixture may be satisfactorily sprayed at a rate of from 4 to 8 lbs. per hour. The spraying may be continued, traversing the gun back and forth across the surface to build up a coating of any desired thickness.

After the coating is applied it is preferably allowed to cool without quenching, and may then be finished by machining or grinding to a desired dimension. The coating thus produced is machinable and may be easily ground. Its machining and grinding characteristics are determined principally by the relatively soft metal included in the powder mixture. It will be appreciated, however, that the machinability and grinding characteristics of the coating are affected to at least some extent by the chromium-nickel-boron alloy, so that those mixtures including relatively high proportions of the chromium-nickel-boron alloys are slightly more difficult to machine and slower to grind than coatings including relatively small proportions of the chromium-nickel-boron alloys.

Coatings formed according to the preferred embodiment of the invention are machinable and may be readily ground. They have excellent corrosion resistance properties and are highly resistant to wear and abrasion. Their wear resistance properties closely approach the wear resistance of surface coatings comprising chromium-nickel-boron alloys alone, yet their cost is substantially less, both because of reduced material cost (stainless steel is generally much cheaper than chromium-nickel-boron alloys) and through a reduction in the cost of finishing the coatings to their final dimensions.

The spraying temperatures of the powder mixtures according to the invention are relatively critical to achieve satisfactory results. On the one hand, at least one of the powder ingredients should be in a plastic state so that its particles can be deformed upon impact to provide an interlocking mechanical bond to secure the coating to the treated surface and a metallurgical bond between the particles of the coating. On the other hand, melting is to be avoided in order to preserve the oil retaining porosity of the coating and the hardness and wear resistance of the chromium-nickel-boron alloy particles.

Equivalent results are not achieved if the powders are pre-alloyed, i. e., if the chromium-nickel-boron alloy is first alloyed by melting with the soft metal and then reduced to powder form and sprayed. Coatings made of such pre-alloys lack the wear resistance of coatings made according to the present invention, because they do not include the discreet, extremely hard particles of the chromium-nickel-boron alloys, which particles appear to be largely responsible for the excellent wear resistance characteristics of coatings according to the invention. For this reason, the spraying temperature is preferably controlled so that the individual powder particles are not molten at the moment of impact so that volume alloying is avoided during the spraying process. The hard alloy particles thus retain their separate identity in the surface coating, and are not dissolved in or diluted by the soft metal to a significant degree.

The particles of at least one, and preferably of both of the metals are highly plastic at the moment of impact so that they "wet" the other particles and become metallurgically bonded, or surface alloyed thereto, and thus produce a strongly cohesive coating.

The soft metal must be one that is capable of "wetting" or of being "wetted" by the hard alloy under these conditions, that is, it must be capable of forming a metallurgical bond with the hard alloy at a temperature below the melting point (liquidus) of the lower melting one of the soft metal and the hard alloy.

In those cases where iron, nickel, or cobalt, or alloys based on iron, nickel, or cobalt are used as the soft metal ingredient it will usually be found that the chromium-nickel-boron alloy has the lower melting point, and will

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accordingly control the choice of a spraying temperature. The chromium-nickel-boron alloys preferred for use in the practice of the invention begin to soften at about 1750° F., and melt at about 1900° F. The upper limit of the spraying temperature (temperature of the powder at the time of impact upon the surface) is therefore about 1900° F., and in practical operation the actual temperature is maintained as close to this temperature as prudence and the nature of the soft metal ingredient permit. If the soft metal has a higher melting point than the chromium-nickel-boron alloy, a temperature of about 1850° F. is used. If the soft metal melts at temperatures below 1850° F. then a lower temperature is preferred, say about 25° to 50° F. below the soft metal melting temperature.

There have thus been described improved metallic coating compositions and methods of spray coating surfaces to protect them against wear, corrosion and abrasion, and to build up undersized parts. Surface coatings according to the invention are porous and highly wear resistant, and their other properties such as corrosion resistance and machinability may be controlled within a broad range of variation.

What is claimed is:

1. A metal spraying composition comprising an intimate mixture in powder form of a hard alloy consisting essentially of chromium, nickel, and boron, and a metal that is relatively soft compared to said alloy, said soft metal being one that is capable of forming a metallurgical bond with said hard alloy at a temperature below the melting point of the lower melting one of said hard alloy and said soft metal, whereby when said composition is spray applied to a workpiece at a temperature within the plastic range but below the liquidus temperature of the lower melting one of said hard alloy and said soft metal the individual particles become metallurgically bonded together to form a cohesive coating in which the hard alloy particles retain their identity.

2. A metal spraying composition consisting essentially of an intimate mixture in powder form of a hard alloy of chromium, nickel, and boron and a metal that is softer than said alloy, said soft metal comprising from 20% to 70% by weight of said mixture and being one that is capable of forming a metallurgical bond with said hard alloy at a temperature below the melting point of the lower melting one of said hard alloy and said soft metal, whereby when said composition is spray applied to a workpiece at a temperature within the plastic range but below the liquidus temperature of the lower melting one of said hard alloy and said soft metal the individual particles become metallurgically bonded together to form a cohesive coating in which the hard alloy particles retain their identity.

3. A metal spraying composition consisting essentially of a mixture of a hard alloy and a soft metal, said alloy and said metal being intermixed in powder form, said hard alloy consisting essentially of:

	Percent
Carbon	0.30 to 1.00
Chromium	8.00 to 18.00
Nickel	65.00 to 85.00
Boron	2.00 to 4.50
Iron	1.25 to 5.50
Silicon	1.25 to 5.50
Cobalt	Up to 1.50

said soft metal being selected from the group consisting of iron, cobalt, nickel, and alloys based on at least one of iron, cobalt, and nickel, whereby when said composition is spray applied to a workpiece at a temperature within the plastic range but below the liquidus temperature of the lower melting one of said hard alloy and said soft metal the individual particles become metallurgically bonded together to form a cohesive coating in which the hard alloy particles retain their identity.

4. A metal spraying composition consisting essentially

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of a mixture of a hard alloy and 18-8 stainless steel, said alloy and said stainless steel being intermixed in powder form, and said hard alloy consisting essentially of:

	Percent
5 Carbon	0.50 to 1.00
Chromium	12.00 to 18.00
Nickel	65.00 to 75.00
Boron	2.50 to 4.50
Iron	3.50 to 5.50
10 Silicon	3.50 to 5.50
Cobalt	Up to 1.00

whereby when said composition is spray applied to a workpiece at a temperature within the plastic range of said hard alloy the individual particles become metallurgically bonded together to form a cohesive coating, and the hard alloy particles retain their separate identity in the coating.

5. A metal spraying composition consisting essentially of a mixture of a hard alloy and a soft metal, said alloy and said metal being intermixed in powder form, said hard alloy consisting essentially of:

	Percent
Carbon	0.50 to 1.00
25 Chromium	12.00 to 18.00
Nickel	65.00 to 75.00
Boron	2.50 to 4.50
Iron	3.50 to 5.50
Silicon	3.50 to 5.50
30 Cobalt	Up to 1.00

said soft metal being selected from the group consisting of iron, cobalt, nickel, and alloys based on at least one of iron, cobalt, and nickel, whereby when said composition is spray applied to a workpiece at a temperature within the plastic range but below the liquidus temperature of the lower melting one of said hard alloy and said soft metal the individual particles become metallurgically bonded together to form a cohesive coating in which the hard alloy particles retain their identity.

6. A metal spraying composition consisting essentially of a mixture of 30% to 80% by weight of a hard alloy and 70% to 20% by weight of a soft metal, said alloy and said metal being intermixed in powder form, said hard alloy consisting essentially of:

	Percent
Carbon	0.30 to 1.00
Chromium	8.00 to 18.00
Nickel	65.00 to 85.00
Boron	2.00 to 4.50
50 Iron	1.25 to 5.50
Silicon	1.25 to 5.50
Cobalt	Up to 1.50

said soft metal being selected from the group consisting of iron, cobalt, nickel, and alloys based on at least one of iron, cobalt, and nickel, whereby when said composition is spray applied to a workpiece at a temperature within the plastic range but below the liquidus temperature of the lower melting one of said hard alloy and said soft metal the individual particles become metallurgically bonded together to form a cohesive coating in which the hard alloy particles retain their identity.

7. A metal spraying composition consisting essentially of an equal weight proportion mixture of a hard alloy and 18-8 stainless steel, said alloy and said stainless steel being intermixed in powder form, and said hard alloy consisting essentially of:

	Percent
Carbon	0.50 to 1.00
70 Chromium	12.00 to 18.00
Nickel	65.00 to 75.00
Boron	2.50 to 4.50
Iron	3.50 to 5.50
Silicon	3.50 to 5.50
75 Cobalt	Up to 1.00

whereby when said composition is spray applied to a workpiece at a temperature within the plastic range of said hard alloy the individual particules become metallurgically bonded together to form a cohesive coating and the hard alloy particles retain their separate identity in the coating.

8. A metal spraying composition consisting essentially of an intimate mixture in powder form of an alloy of chromium, nickel, and boron and a metal that is softer than said alloy, said soft metal comprising from 20% to 70% by weight of said mixture and being one that is capable of forming a metallurgical bond with said hard alloy at a temperature below the melting point of the lower melting one of said hard alloy and said soft metal, said mixture having a particle size distribution of 100% through an 80 mesh screen, 99% through a 120 mesh screen, and less than 45% through a 325 mesh screen, whereby when said composition is spray applied to a workpiece at a temperature within the plastic range but below the liquidus temperature of the lower melting one of said hard alloy and said soft metal the individual particles become metallurgically bonded together to form a cohesive coating in which the hard alloy particles retain their identity.

9. A metal spraying composition consisting essentially of a mixture of a hard alloy and a soft metal, said alloy and said metal being intermixed in powder form, said hard alloy consisting essentially of:

	Percent
Carbon -----	0.50 to 1.00
Chromium -----	12.00 to 18.00
Nickel -----	65.00 to 75.00
Boron -----	2.50 to 4.50
Iron -----	3.50 to 5.50
Silicon -----	3.50 to 5.50
Cobalt -----	Up to 1.00

said soft metal being selected from the group consisting of iron, cobalt, nickel, and alloys based on at least one of iron, cobalt, and nickel, said mixture having a particle size distribution of 100% through an 80 mesh screen, 99% through a 120 mesh screen, and less than 45% through a 325 mesh screen, whereby when said composition is spray applied to a workpiece at a temperature within the plastic range but below the liquidus temperature of the lower melting one of said hard alloy and said soft metal the individual particles become metallurgically bonded together to form a cohesive coating in which the hard alloy particles retain their identity.

10. A metal spraying composition consisting essentially of an equal weight proportion mixture of a hard alloy and 18-8 stainless steel, said alloy and said stainless steel being intermixed in powder form, and said hard alloy consisting essentially of:

	Percent
Carbon -----	0.50 to 1.00
Chromium -----	12.00 to 18.00
Nickel -----	65.00 to 75.00
Boron -----	2.50 to 4.50
Iron -----	3.50 to 5.50
Silicon -----	3.50 to 5.50
Cobalt -----	Up to 1.00

said mixture having a particle size distribution of 100% through an 80 mesh screen, 99% through a 120 mesh screen, and less than 45% through a 325 mesh screen, whereby when said composition is spray applied to a workpiece at a temperature within the plastic range of said hard alloy the individual particles become metallurgically bonded together to form a cohesive coating and the hard alloy particles retain their separate identity in the coating.

11. Method of forming a porous metallic surface coat-

ing comprising the step of spraying upon a surface to be coated a mixture in powder form of a hard alloy of chromium, nickel, and boron and a metal that is relatively soft compared to said alloy, at an elevated temperature at which at least one of said metal and said alloy is plastic but below the melting temperatures of said alloy and said metal, said soft metal being capable of forming a metallurgical bond with said hard alloy at said temperature, thereby to form a wear resistant and machinable cohesive surface coating in which the particles of said hard alloy retain their identity and are metallurgically bonded to said soft metal.

12. Method of forming a porous metallic surface coating comprising the step of spraying upon a surface to be coated a mixture in powder form of 30% to 80% by weight of a hard alloy of chromium, nickel, and boron and 70% to 20% by weight of a metal that is relatively soft compared to said alloy, at an elevated temperature at which at least one of said metal and said alloy is plastic but below the melting temperatures of said alloy and said metal, said soft metal being capable of forming a metallurgical bond with said hard alloy at said temperature, thereby to form a wear resistant and machinable cohesive surface coating in which the particles of said hard alloy retain their identity and are metallurgically bonded to said soft metal.

13. Method of forming a porous metallic surface coating comprising the steps of spraying upon a surface to be coated a mixture in powder form of a hard alloy and a soft metal, said hard alloy consisting essentially of:

	Percent
Carbon -----	0.30 to 1.00
Chromium -----	8.00 to 18.00
Nickel -----	65.00 to 85.00
Boron -----	2.00 to 4.50
Iron -----	1.25 to 5.50
Silicon -----	1.25 to 5.50
Cobalt -----	Up to 1.50

said soft metal being selected from the group consisting of iron, cobalt, nickel, and alloys based on at least one of iron, cobalt, and nickel, and heating said mixture so that it is at a temperature of about 1750° F. to 1900° F. when it impinges upon said surface, thereby to form a wear resistant and machinable cohesive surface coating in which the particles of said hard alloy retain their identity and are metallurgically bonded to said soft metal.

14. Method of forming a porous metallic surface coating comprising the steps of spraying upon a surface to be coated a mixture in powder form of a hard alloy and a soft metal, said hard alloy consisting essentially of:

	Percent
Carbon -----	0.30 to 1.00
Chromium -----	8.00 to 18.00
Nickel -----	65.00 to 85.00
Boron -----	2.00 to 4.50
Iron -----	1.25 to 5.50
Silicon -----	1.25 to 5.50
Cobalt -----	Up to 1.50

said soft metal being selected from the group consisting of iron, cobalt, nickel, and alloys based on at least one of iron, cobalt, and nickel, and heating said mixture during said spraying to a temperature of about 1850° F., thereby to form a wear resistant and machinable cohesive surface coating in which the particles of said hard alloy retain their identity and are metallurgically bonded to said soft metal.

15. Method of forming a porous metallic surface coating comprising the steps of spraying upon a surface to be coated a mixture in powder form of 30% to 80% by

weight of a hard alloy and 70% to 20% by weight of a soft metal, said alloy consisting essentially of:

	Percent
Carbon -----	0.30 to 1.00
Chromium -----	8.00 to 18.00
Nickel -----	65.00 to 85.00
Boron -----	2.00 to 4.50
Iron -----	1.25 to 5.50
Silicon -----	1.25 to 5.50
Cobalt -----	Up to 1.50

said soft metal being selected from the group consisting of iron, cobalt, nickel, and alloys based on at least one of iron, cobalt, nickel, and heating said mixture while it is being sprayed to a temperature of about 1750° F. to 1900° F., thereby to form a wear resistant and machinable cohesive surface coating in which the particles of said hard alloy retain their identity and are metallurgically bonded to said soft metal.

16. Method of forming a porous metallic surface coating comprising the steps of spraying upon a surface to be coated an equal weight proportion mixture in powder form of a hard alloy and 18-8 stainless steel, said hard alloy consisting essentially of:

	Percent
Carbon -----	0.30 to 1.00
Chromium -----	8.00 to 18.00
Nickel -----	65.00 to 85.00
Boron -----	2.00 to 4.50
Iron -----	1.25 to 5.50
Silicon -----	1.25 to 5.50
Cobalt -----	Up to 1.50

and heating said mixture during said spraying to a temperature of about 1750° F. to 1900° F., thereby to form a wear resistant and machinable cohesive surface coating in which the particles of said hard alloy retain their identity and are metallurgically bonded to said stainless steel.

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