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(54) **Corrosion resistant self-fluxing alloys for thermal spraying.**

(57) A novel alloy is disclosed which is characterized by high resistance to wear and corrosion. The alloy consists essentially of up to 25% chromium, 10 to 28% molybdenum, 0.5 to 18% tungsten, 0.1 to 10% copper, 2 to 8% boron, 2.5 to 8% silicon, and up to 3% carbon; the balance being incidental impurities and at least 30% of a metal selected from the group consisting of nickel, cobalt and combinations thereof, wherein the total of boron and carbon is at least 2.5%. The alloy is preferably in the form of a powder for thermal spraying, and coatings produced thereby may be subsequently fused.

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CORROSION RESISTANT SELF-FLUXING ALLOYS FOR THERMAL SPRAYING

This invention relates to a self-fluxing alloy composition characterized by improved wear and corrosion resistance and to a process for thermal spraying such alloy.

Background of the Invention

Self-fluxing alloys of nickel and cobalt are quite common for hard facing coatings. They contain boron and silicon which act as fluxing agents during the coating operation and as hardening agents in the coating. A common method of processing such alloys is by thermal spraying.

Thermal spraying, also known as flame spraying, involves the heat softening of a heat fusible material such as metal or ceramic, and propelling the softened material in particulate form against a surface which is to be coated. The heated particles strike the surface and bond thereto. A conventional thermal spray gun is used for the purpose of both heating and propelling the particles. In one type of thermal spray gun, the heat fusible material is supplied to the gun in powder form. Such powders are typically comprised of small particles, e.g., between 100 mesh U. S. standard screen size (149 microns) and about 2 microns.

A thermal spray gun normally utilizes a combustion or plasma flame to produce the heat for melting of the powder particles. It is recognized by those of skill in the art, however, that other heating means may be used as well, such as electric arcs, resistance heaters or induction heaters, and these may be used alone or in combination with other forms of heaters. In a powder-type combustion thermal spray gun, the carrier gas, which entrains and transports the powder, can be one of the combustion gases or an inert gas such as nitrogen, or it can be simply compressed air. In a plasma spray gun, the primary plasma gas is generally nitrogen or argon. Hydrogen or helium is usually added to the primary gas. The carrier gas is generally the same as the primary plasma gas, although other gases, such as hydrocarbons, may be used in certain situations.

The material alternatively may be fed into a heating zone in the form of a rod or wire. In the wire type thermal 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, such as a combustion flame, 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. In an arc wire gun two wires are melted in an electric arc struck between the wire ends, and the molten metal is atomized by compressed gas, usually air, and sprayed to a workpiece to be coated. The rod or wire may be conventionally formed as by drawing, or may be formed by sintering together a powder, or by bonding together the powder by means of an organic binder or other suitable binder which disintegrates in the heat of the heating zone, thereby releasing the powder to be sprayed in finely divided form.

Usually self-fluxing alloys are applied in two steps, namely thermal sprayed in the normal manner and then fused in situ with an oxyacetylene torch, induction coil, furnace or the like. The fluxing agents make the fusing step practical in open air. However, the alloys may also be thermal sprayed with a process such as plasma spraying without requiring the fusing step, but the coatings are not quite as dense or wear resistant. Generally self-fluxing alloy coatings are used for hard surfacing to provide wear resistance, particularly where a good surface finish is required since the fusing produces a coating having very low porosity.

A typical self-fluxing alloy composition of nickel or cobalt contains chromium, boron, silicon and carbon. An alloy may additionally contain molybdenum, tungsten and/or iron. For example U. S. Patent No. 2,868,639 discloses an alloy for hard surfacing composed of (by weight) 7 to 17% chromium, 1 to 4.5% boron, 1 to 5.5% silicon, 0.1 to 5.5% iron, 6 to 20% of at least one of tungsten and molybdenum, 0.05 to 2.5% carbon, the remainder nickel and incidental impurities. Similarly, U. S. Patent No. 2,936,229 discloses a cobalt alloy containing 1.5 to 4% boron, 0 to 4% silicon, 0 to 3% carbon, 0 to 20% tungsten and 0 to 8% molybdenum.

U. S. Patent No. 2,875,043 teaches a spray-weldable alloy containing at least 40% nickel, 1 to 6% boron, silicon up to about 6%, 3 to 8% copper and 3 to 10% molybdenum. Tungsten is not included.

U. S. Patent No. 3,471,310 discloses a variety of "typical" alloys. One contains molybdenum, silicon, copper, chromium, iron, tungsten, balance nickel, but no boron (column 4, lines 3-10). Another contains boron and copper but no molybdenum or tungsten (column 4, lines 34-41). This patent is directed to cladding such alloy powders with a flux using a resin. A variety of illustrative examples of fluxes in compound form are provided (column 8, lines 33-54).

European Patent Specification No. 0 009 881 (published January 11, 1984) involves an alloy composition of at least 48% cobalt, nickel and (if present) iron; 27 to 35% chromium; 5 to 15% molybdenum and/or tungsten; 0.3 to 2.25% carbon and/or boron; 0 to 3% silicon and/or manganese; 0 to 5% titanium and the like; 0 to 5% copper; and 0 to 2% rare earths. There are, however, certain restrictions including that if there is 2% or more of carbon and/or boron present, there is more than 30% chromium present. More than 10% iron is preferred. Also, preferably no boron is present or, if it is present, it should not constitute more than 1% of the composition; and further limitations on boron are indicated where a significant amount of carbon is present.

U. S. Patent No. 4,116,682 describes a class of amorphous metal alloys of the formula MaTbXc wherein M may be iron, cobalt, nickel and/or chromium, T may include molybdenum and tungsten, X may include boron, silicon and carbon and a,b and c represent the respective atomic proportions. The group X of boron, etc. has a maximum of 10 atomic percent which calculates to about 1.9% by weight for boron in the amorphous alloys; thus boron is characteristically low compared to the boron content in self-fluxing type of alloys, although there is some overlap.

Some of the above-indicated alloys have been in use commercially for more than 25 years and have been quite successful. However, if very high wear resistance is needed a carbide such as tungsten carbide is added as described, for example, in British Patent No. 867,455. These carbide-containing alloys are expensive, difficult to grind finish, harder to fuse and less resistant to corrosion.

In view of the foregoing, a primary object of the present invention is to provide a novel alloy composition characterized by both corrosion resistance and wear resistance.

A further object of this invention is to provide an improved self-fluxing alloy for the thermal spray process.

Another object is to provide an improved thermal spray process for producing corrosion and wear resistant coatings.

Brief Description of the Invention

The foregoing and other objects are achieved by an alloy composition of up to 25% chromium, 10 to 28% molybdenum, 0.5 to 18% tungsten, 0.1 to 10% copper, 2 to 8% boron, 2.5 to 8% silicon and up to 3% carbon; the balance being incidental impurities and at least 30% of a metal selected from the group consisting of nickel, cobalt and combinations thereof, wherein the total of boron and carbon is at least 2.5%.

Detailed Description of the Invention

According to the present invention, an alloy material has been developed which has a high degree of resistance to both wear and corrosion. The alloy is especially suitable for thermal spraying onto metallic substrates by conventional thermal spray equipment, and the coatings optionally may be subsequently fused.

The alloy composition of the present invention is broadly in the ranges of, by weight:

up to 25% chromium,
10 to 28% molybdenum,
0.5 to 18% tungsten,
0.1 to 10% copper,
2 to 8% boron,
2.5 to 8% silicon,
up to 3% carbon;
the balance being incidental impurities and at least 30% of a metal selected from the group consisting of nickel, cobalt and combinations thereof, and the total of boron and carbon being at least 2.5%.

Preferably the ranges are as follows:

2 to 23% chromium,
10 to 25% molybdenum,
0.5 to 10% tungsten,
0.1 to 8% copper,
2.5 to 6% boron,

2.5 to 5.5% silicon, and
0.5 to 2% carbon;
the balance being incidental impurities and at least 30% of a metal selected from the group consisting of nickel, cobalt and combinations thereof.

Most preferably the composition is:
15 to 20% chromium,
15 to 20% molybdenum,
1 to 4% tungsten,
1 to 4% copper,
3 to 5% boron,
3 to 5% silicon,
0.5 to 1% carbon, and
balance nickel and incidental impurities.

In order to maintain a high corrosion resistance, total content of iron should be kept to a minimum value and should be generally less than about 1.0% by weight and preferably less than about 0.5%.

Nickel is generally preferable but cobalt may be substituted partially or fully to provide coating performance benefits depending upon service requirements such as resistance to certain high temperature corrosive conditions.

Optional elements that may be included in the composition are zirconium, tantalum, niobium, titanium, vanadium and hafnium, totalling up to about 7% by weight, to form carbides and further improve corrosion resistance. Other optional elements may be manganese, phosphorous, germanium and arsenic, totalling up to about 3%, to reduce melting point and improve fusing; and rare earth elements such as yttrium and/or cerium, totalling up to about 2%, for additional oxidation and wear resistance. Otherwise incidental impurities should be less than about 2% and preferably less than 0.5%.

Although the composition of the present invention may be quite useful in cast or sintered form or the like, it is especially suitable for application as a coating such as by welding, transferred arc or, preferably, thermal spraying.

It is important that the composition be in alloy form in order to obtain the desirable benefit of the homogeneity available therefrom. Alloy powder of size and flowability suitable for thermal spraying is one such form. Such powders should fall in the range between 100 mesh (U. S. standard screen size) (149 microns) and about 2 microns.

The powders are sprayed in the conventional manner, using a powder-type thermal spray gun, although it is also possible to combine the same into the form of a composite wire or rod, using plastic or a similar binder, as for example, polyethylene or polyurethane, which decomposes in the heating zone of the gun. Alloy rods may also be used in the wire thermal spray processes. The rods or wires should have conventional sizes and accuracy tolerances for flame spray wires and thus, for example, may vary in size between 6.4 mm and 20 gauge.

The alloy of the present invention may be used in its as-sprayed condition, where preferably plasma spraying is used. In such case, the powder size should be somewhat fine, for example between 270 mesh - (53 microns) and 2 microns.

Alternatively the coating may be fused in the ordinary manner of a self-fluxing alloy. The starting powder for such purpose may be sized as indicated above for as-sprayed use or, for thicker coatings, coarser powder such as between 140 and 325 mesh (105 and 44 microns). Fusing temperature is estimated to be about 1100 to 1250 degrees centigrade.

Alloy coatings of the present invention are particularly dense and low in oxide content, and show significant improvements in both wear resistance and corrosion resistance over prior coatings. The coatings are excellently suited as bearing and wear surfaces on machine components, particularly where there are corrosive conditions as, for example, for coating petrochemical production equipment such as pump plungers, sucker rod couplings, sleeves, mud pump liners, and compressor rods; the circumference of automotive and diesel engine piston rings and cylinder walls; the interior surfaces of flue gas scrubbers for power generation and process industries; pulp and paper processing equipment such as digestors, de-barking machines, and recovery boilers; glass manufacturing equipment such as molds, mold plates, plungers, and neck rings; electric power generation boiler water walls, slope tubes, control valves, and pump components; gas turbine engine components such as nozzles and stator vane segments; machine ways; printing rolls; electroplating fixtures; rotary engine trochoids, seals and end plates; engine crankshafts;

roll journals; bearing sleeves; impeller shafts; gear journals; fuel pump rotors; screw conveyors; wire or thread capstans; shifter forks; doctor blades; farming tools; motor shafts; lathe and grinder centers; cam followers.

Example 1

An alloy powder of the following composition by weight was prepared by nitrogen atomization from the melt:

17.2% chromium
18.7% molybdenum
2.5% tungsten
2.0 copper
0.6% iron
3.7% boron
3.9% silicon
0.5% carbon
Balance nickel and incidental impurities

The powder was sized to about -270 mesh (53 microns) +2 microns. It was thermal sprayed with a plasma gun of the type described in U. S. Patent No. 3,145,287 and sold by Metco as Type 7MB with a #6 powder port and GE nozzle, using the following parameters: nitrogen primary gas at 3.5 bar pressure and 95 standard 1/min flow, hydrogen secondary gas at 3.5 bar pressure and 5.7 1/min flow, arc at 85 to 90 volts and 300 amperes, powder feed rate 6 kg/hr using nitrogen carrier gas at 10 1/min, and spray distance 13 cm. Substrate was cold rolled steel prepared by grit blasting in the normal manner.

Coatings up to 0.6 mm thick were produced. These as-sprayed coatings were ground as for common self-fluxing alloy coatings to a finish of 8 to 15 microinches (arithmetic average). Hardness was Rc 55.

Example 2

The following nickel alloys, outside the realm of the present invention, were similarly prepared and sprayed (Table 1).

Table 1

	WEIGHT PERCENT			
Alloy:	2a	2b	2c	2d
Chromium	16.2	17.7	16.2	17.7
Molybdenum	19.3	19.8	19.7	10.7
Tungsten	1.6	--	2.4	2.5
Copper	--	2.1	2.0	2.2
Iron	0.5	0.7	0.06	0.6
Boron	3.5	3.8	2.8	2.7
Silicon	4.4	3.7	3.8	4.0
Carbon	0.5	0.6	0.7	0.6

Example 3

The alloy powder of Example 1 was similarly sprayed and then it was fused with an oxyacetylene torch. The coating had hardness of Rc 70 and a microhardness of DPH(300) 998.

The alloy coatings of Examples 1 and 2 were tested for corrosion resistance by removing the coatings from the substrates and exposing them to 25% sulfuric acid solution at 80 degrees centigrade for 3 hours. The Example 1 alloy and alloys 2b, 2c, and 2d showed a corrosion rate of about 0.1 to 0.2 inches per year; alloy 2a showed a surprisingly high rate of about 4 inches per year. There was obvious discoloration of the liquid for the alloy 2a test, whereas the others remained nearly clear.

Microhardness determined for Examples 1 and 2 are given in Table 2, using a DPH 300 indenter.

Table 2

Alloy	DPH 300	Av. No. Cracks per indentation	Av. Longest (microns)
Example 1	791	3.7	19.5
2a	746	4.9	25.7
2b	549	8.3	49.7
2c	741	5.5	19.2
2d	656	5.5	21.1

These hardnesses are highest for the alloy of the present invention and are significantly lower for the low-molybdenum alloy and are especially low for the tungsten-free alloy. Microscopic examination revealed a corrolation to microcracking near the indentation as further shown in Table 1, in terms of the average number of cracks per diamond indentation and the average length of the longest crack for each of the 13 to 17 indentations measured. This particularly indicates an unexpected susceptibility of the tungsten-free alloy to microcracking under point loading, a factor in abrasive wear.

Abrasive wear resistance for Examples 1 and 3 of the present invention was measured by placing coated samples in sliding motion against a cast iron plate with a slurry of 150 gms of between 270 mesh - (53 microns) and 15 microns aluminum oxide abrasive powder in 500 ml of water. A load of 3.3 kg/cm^2 was applied and the surface motion was about 122 cm/sec for 20 minutes. Coating loss was determined.

The coating of Example 1, which was not subsequently fused, showed an abrasive wear resistance comparable to that of a fused coating of thermal sprayed AMS 4775A which is considered to be an industry standard. Surprisingly, the wear resistance of the fused coating of Example 3 was greater than that of the fused AMS 4775A alloy coating containing 50% tungsten carbide according to aforementioned British Patent No. 867,455.

Sliding wear data for the alloy of Example 1 was determined with an Alpha LFW-1, friction and wear testing machine sold by Fayville-Levalle Corp., Downers Grove, I11., using a 3.5 cm diameter test ring and 45 kg load at 197 RPM, for 12,000 revolutions.

Results in comparison to molybdenum coatings thermal sprayed with the wire process are set forth in Table 3; such molybdenum coatings are used virtually universally on automotive piston compression rings. The data show improved friction against hard steel and a substantial improvement in the wear of the ring surface of both hard steel and cast iron.

TABLE 3

	Example 1	Molybdenum
Ring surface: hard steel Rc 60		
Average friction coefficient	0.12	0.15
Peak friction coefficient	0.16	0.20
Coating wear (scar width, mm)	1.0	1.2
Ring wear (weight loss, mg)	0.3	1.2
Ring surface: cast iron Rb 79		
Average friction coefficient	0.18	0.16
Peak friction coefficient	0.20	0.20
Coating wear (scar width, mm)	0.9	1.0
Ring wear (weight loss, mg)	2.2	16.3

While the invention has been described above in detail with reference to specific embodiments, various changes and modifications which fall within the spirit of the invention and scope of the appended claims will become apparent to those skilled in this art. The invention is therefore only intended to be limited by the appended claims or their equivalents.

Claims

1. An alloy characterized by high resistance to wear and corrosion, consisting essentially of, as percent by weight:
Up to 25% chromium,
10 to 28 molybdenum,
0.5 to 18% tungsten,
0.1 to 10% copper,
2 to 8% boron,
2.5 to 8% silicon, and
up to 3% carbon;
the balance being incidental impurities and at least 30% of a metal selected from the group consisting of nickel, cobalt and combinations thereof; the total of boron and carbon being at least 2.5%.

2. An alloy characterized by high resistance to wear and corrosion, consisting essentially of, as percent by weight:
15 to 20% chromium,
15 to 20% molybdenum,
1 to 4% tungsten,
1 to 4% copper,
3 to 5% boron,
3 to 5% silicon,
0.5 to 1% carbon, and
balance nickel and incidental impurities.

3. The alloy of Claim 1 or 2 wherein, if present, iron is less than about 0.5%.

4. The alloy of Claim 1 or 2 additionally including a total of up to about 7% of one or more elements selected from the group consisting of zirconium, tantalum, niobium, titanium, vanadium and hafnium.

5. The alloy of Claim 1 or 2 additionally including a total of up to about 3% of one or more elements selected from the group consisting of manganese, phosphorous, germanium and arsenic.

6. The alloy of Claim 1 or 2 additionally including a total of up to about 2% of rare earth elements.

7. The alloy of Claim 1 or 2 wherein the composition is in the form of a thermal spray alloy powder.

8. A thermal spray powder of an alloy characterized by high resistance to wear and corrosion, consisting essentially of, as percent by weight:
15 to 20% chromium,
15 to 20% molybdenum,
1 to 4% tungsten,
1 to 4% copper,
3 to 5% boron,
3 to 5% silicon,
0.5 to 1% carbon, and
up to 0.5% iron;
up to about 7% total of one or more first elements selected from the group consisting of zirconium, tantalum, niobium, titanium, vanadium and hafnium;
up to about 3% total of one or more second elements selected from the group consisting of silicon, manganese, phosphorous, germanium and arsenic;
up to about 2% total of rare earth elements; and
balance nickel and incidental impurities.

9. A thermal spray process comprising the step of thermal spraying the alloy of Claim 1 to produce a coating.

10. A thermal spray process comprising the step of thermal spraying the alloy of Claim 2 to produce a coating.

11. A thermal spray process comprising the step of thermal spraying the powder of Claim 8 to produce a coating.

12. The process of Claim 8 or 9 or 11 further comprising the step of fusing the coating.

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 86 11 5143

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A,D	US-A-2 868 639 (GONSER) * Claims 1-5 * ---	1,2,9, 10	C 22 C 19/05 C 23 C 4/08
A	GB-A-1 016 629 (DEUTSCHE EDELSTAHLWERKE AG) * Claims 1,5-10 * ---	1,2,9, 10	
A,D	US-A-2 936 229 (SHEPARD) * Claims 1,15,16; column 2, lines 11-49 * ---	1,2,9, 10	
A,D	US-A-2 875 043 (TOUR) * Clams 1-6,11 * ---	1,2,9, 10	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	DE-B-1 758 869 (WOOCK) * Claims 1-5 * ---	1	C 22 C C 23 C
A	GB-A-1 049 724 (BIRMINGHAM SMALL ARMS C. LTD) * Claims 1-3 * -----	1,2,4, 5	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23-02-1987	LIPPENS M.H.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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