



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : B22F 1/00, 7/06	A1	(11) International Publication Number: WO 94/17940 (43) International Publication Date: 18 August 1994 (18.08.94)
(21) International Application Number: PCT/US94/01076 (22) International Filing Date: 27 January 1994 (27.01.94) (30) Priority Data: 08/012,709 3 February 1993 (03.02.93) US (71) Applicant: KENNAMETAL INC. [US/US]; P.O. Box 231, Latrobe, PA 15650 (US). (72) Inventor: TERRY, Charles, J.; 3155 Alcorn Road, Fallon, NV 80406 (US). (74) Agents: PRIZZI, John, J. et al.; Kennametal Inc., P.O. Box 231, Latrobe, PA 15650 (US).		(81) Designated States: AU, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: SPRAY POWDER FOR HARDFACING AND PART WITH HARDFACING		
(57) Abstract		
A spray powder for thermal spraying onto a substrate to provide a hardfacing, and a part with such hardfacing on the surface thereof, that is corrosion-resistant and abrasion-resistant. The spray powder comprises between about 75 to about 90 weight percent of tungsten carbide. The powder further comprises between about 10 and 25 weight percent of a nickel-based alloy, which includes Mo, and optionally, includes one or more of Fe, C, Cr, Mn, Co, Si and W.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

-1-

SPRAY POWDER FOR HARDFACING AND PART WITH HARDFACING
BACKGROUND OF THE INVENTION

The invention pertains to a spray powder which is sprayed, such as by thermal spraying techniques, onto the surface of the substrate to form a hardfacing on the substrate surface, as well as a part having such hardfacing thereon. More specifically, the invention pertains to the aforementioned spray powder which has excellent abrasion-resistant properties and excellent corrosion-resistant properties, as well as a part with such hardfacing thereon thereby having excellent abrasion-resistant properties and excellent corrosion-resistant properties.

Heretofore, spray powders have been used to form hardfacing on the surface of a substrate, such as a part, so as to protect the substrate from abrasion and corrosion. For example, Kennametal Inc., of Latrobe, Pennsylvania (assignee of the present application) has heretofore made and sold a tungsten carbide-cobalt-chromium spray powder which produces a layer on a substrate with abrasion resistance and corrosion resistance.

The patent literature contains a number of patents which concern hardfacing alloys. For example, U.S. Patent No. 4,013,453, to Patel, concerns a tungsten carbide-nickel powder hardfacing alloy. The alloy starts with two basic components; namely, a WC-Ni mixture and a nickel alloy (2.5-20% Cr, 0.5-6% Si,

0.5-5% B, up to 10% Fe, and the balance Ni). In the final alloy, the average WC content is between 10 to 30%. U.S. Patent No. 4,526,618, to Keshavan et al., concerns an abrasion-resistant spray coating comprising
5 (1) 78 to 88 wt% tungsten carbide, and (2) an alloy with 6-18% boron, 0-6% Si, 0-20% Cr, 0-5% Fe and the balance nickel. U.S. Patent No. 3,725,017, to Prasse et al., concerns a hardfacing comprising a boron-hardened tungsten phase in a matrix of nickel-chromium
10 or nickel-aluminum. The '017 patent discloses the use of powders of tungsten carbide, boron and at least one alloying element (one or more of Co, Ni, Cr and Al) to produce the boron-hardened tungsten phase. U.S. Patent No. 4,996,114, to Darrow, concerns a coating process
15 and the resultant coating. The process comprises two basic steps. For the first step, one applies a coating of a binder (Co or Ni) and carbide grit to the surface of the substrate. The second step comprises carbiding, nitriding or boriding the surface so as to harden the
20 surface of the binder without affecting the carbides. U.S. Patent No. 4,124,737, to Wolfa et al., concerns a high temperature wear resistant coating comprising a Co-based alloy containing 17-35% Cr, 5-20% Ta, 0-2% Y, 0.25% Si, 0-3.0% Mn, 0.5-3.5% C, 0-14% Al and 0-50% of
25 at least one metal oxide (such as alumina). U.S. Patent No. 4,414,029, to Newman et al., concerns a welding rod filler of macrocrystalline WC along with niobium alone or in combination molybdenum for use as a hardfacing.

30 While earlier spray powders have provided some degree of abrasion resistance and corrosion resistance, there has been a need to provide a spray powder with excellent abrasion-resistant properties in
35 combination with excellent corrosion-resistant properties. Typical parts which require surface layers with excellent abrasion-resistant and excellent corrosion-resistant properties include the wetted parts

in a chemical processing slurry pump which experience wear. Other typical parts include downhole drilling parts which experience wear and are in contact with "sour gas," i.e., hydrogen sulfide.

5 The patent literature contains patents which disclose hardfacing layers which are supposed to provide corrosion-resistant properties. For example, U.S. Patent No. 4,064,608, to Jaeqer, concerns a ferrous roll with a hardfacing alloy that is supposed
10 to be heat, corrosion and wear resistant. The alloy may be nickel-base, iron-base or cobalt-base and include 0.5-5% B, 0.5-6% Si, and up to 3% carbon along with carbide formers such as W, Cr and Mo. U.S. Patent
15 No. 4,822,415, to Dorfman et al., concerns an iron-based thermal spray powder. According to the '415 patent, the goal of the powder is to provide an alloy with corrosion resistance, frictional wear resistance and abrasive wear resistance. The composition
20 comprises 0-40% Cr, 1-40% Mo, 1-15% Cu, 0.2-5% B, 0-5% Si, 0.01-2% C, and the balance impurities with at least 30% Fe. The spray alloy does not contain WC.

Even though earlier patents mention corrosion-resistant hardfacing alloys, there remains the need to provide a spray powder for application as a
25 hardfacing which has excellent abrasion-resistant properties and excellent corrosion-resistant properties.

SUMMARY OF THE INVENTION

It is the primary object of the invention to
30 provide a spray powder for application as a hardfacing which has excellent abrasion-resistant properties and excellent corrosion-resistant properties.

It is another object of the invention to
35 provide a part on the surface of which there is a hardfacing so as to provide the part with excellent abrasion-resistant and corrosion-resistant properties.

In one form thereof, the invention is a sintered spray powder for application as a corrosion-resistant hardfacing on a substrate comprising the following constituents: WC in an amount between about 75 and about 90 weight percent of the sintered powder; Mo in an amount of between about 1.6 and about 7.5 weight percent of the sintered powder; Fe in an amount of between 0 and about 2 weight percent of the sintered powder; C, other than C combined in WC, in an amount of between 0 and about 0.03 weight percent of the sintered powder; Cr in an amount of between 0 and about 4.4 weight percent of the sintered powder; Mn in an amount of between 0 and about .25 weight percent of the sintered powder; Co in an amount of between 0 and about .63 weight percent of the sintered powder; Si in an amount of between 0 and about .25 weight percent of the sintered powder; W, other than W combined in WC, in an amount of between 0 and about 1.4 weight percent of the sintered powder; and the balance nickel, wherein at least about 3.4 weight percent of the sintered powder is nickel.

In another form thereof, the invention is a sintered spray powder comprising the following constituents: about 80 weight percent of tungsten carbide; between about 3.2 and about 6 weight percent Mo; between 0 and about 1.6 weight percent Fe; between 0 and about .0024 weight percent C, other than C combined in WC; between 0 and about 3.5 weight percent Cr; between 0 and about .2 weight percent manganese; between 0 and about .5 weight percent cobalt; between 0 and about .2 weight percent Si; between 0 and about 1.06 weight percent tungsten metal, other than tungsten combined in WC; and the balance nickel, wherein at least about 6.8 weight percent of the powder is nickel.

In still another form, the invention is a sintered spray powder comprising the following constituents: about 88 weight percent of tungsten

carbide; between about 1.9 and about 3.6 weight percent Mo; between 0 and about 1 weight percent Fe; between 0 and about .015 weight percent C, other than C combined in WC; between about 0 and about 2.1 weight percent Cr; between 0 and about .12 weight percent manganese; between 0 and about .3 weight percent cobalt; between 0 and about .12 weight percent Si; between 0 and about .64 weight percent tungsten metal, other than tungsten combined in WC; and the balance nickel, wherein at least about 4.1 weight percent of the powder is nickel.

In still another form thereof, the invention is a part having a surface with hardfacing thereon, the hardfacing comprising: WC in an amount between about 75 and about 90 weight percent; Mo in an amount of between about 1.6 and about 7.5 weight percent; Fe in an amount of between 0 and about 2 weight percent; C, other than C combined in WC, in an amount of between 0 and about 0.03 weight percent; Cr in an amount of between 0 and about 4.4 weight percent; Mn in an amount of between 0 and about .25 weight percent; Co in an amount of between 0 and about .63 weight percent; Si in an amount of between 0 and about .25 weight percent; W, other than W combined in WC, in an amount of between 0 and about 1.4 weight percent; and the balance nickel, wherein at least about 3.4 weight percent is nickel.

DETAILED DESCRIPTION OF SPECIFIC EMBODIMENTS

The invention pertains to a spray powder for application as a hardfacing that presents excellent corrosion-resistant properties and excellent abrasion-resistant properties. The invention also pertains to an article of manufacture, such as a wear part or the like, that could be subject to abrasive and corrosive conditions and which includes a surface with the hardfacing applied thereon. The combination of these properties becomes important for articles such as wear parts that operate in a corrosive environment.

Typical parts which require both abrasion-resistant and corrosion-resistant surface layers include the wetted parts in a chemical processing slurry pump which experience wear. Other typical parts
5 include downhole drilling parts which experience wear and are in contact with corrosive brine or "sour gas," i.e., hydrogen sulfide, which has a corrosive action on the parts.

In addition to the above articles, the
10 hardfacing could be applied to centrifugal pump shaft bearing surfaces, pump liners, mud pump valve seats, coal slurry pump valve seats, bearing surfaces on impellers in centrifugal pumps, radial shaft support surfaces in centrifugal pumps, thrust areas in
15 centrifugal pumps, the clapper of a check valve in valve seats, crude pipeline, pump impellers, mixing impellers for mixing and blending slurries, gate valves and various valve components, liners for pistons in drilling pumps, tool joints and casing for downhole
20 drilling, directional bits and drill motors, impeller stages in elevated submersible pumps, down hole hydraulic jet pump throats, refractory/ceramic liners to vessels and pipelines for petrochemicals, cutterfacings or composite rods for junk mills, and
25 injection nozzles.

The hardfacing is applied via plasma or HVOF (high velocity oxygen fuel) spraying techniques. The following patents discuss flame spraying techniques that may be suitable for use with the spray powder of
30 the present invention: U.S. Patent Nos. 2,714,563; 2,858,411; 2,950,867; 3,016,447 and 3,190,560

The present invention comprises the sintered product of a combination of a wear-resistant tungsten carbide and a corrosion-resistant nickel-based alloy.
35 The specific tungsten carbide in the examples is available from Kennametal Inc. of Latrobe, Pennsylvania, USA, as the traditional APT-based

tungsten carbide. However, the present scope of the invention encompasses macrocrystalline tungsten carbide available from Kennametal Inc., of Latrobe, Pennsylvania.

5 The specific nickel-based alloy is NISTELLE C powder, available from the Stellite Division of Haynes International, Inc. The NISTELLE C has a composition of 16-18 wt% Mo; 13-17.5 wt% Cr; 3.7-5.3 wt% W; 4.5-7 wt% Fe; and the balance Ni. However, applicant intends
10 the scope of the invention to be broader than the use of these specific alloys.

 Applicant has found that a combination of tungsten carbide and the nickel-based alloy produces a spray powder useful for hardfacing that produces a
15 hardfacing with excellent corrosion-resistant and abrasion-resistant properties. In regard to one specific embodiment of the spray powder, about 80 weight percent traditional APT-based tungsten carbide (available from Kennametal Inc., of Latrobe,
20 Pennsylvania) and about 20 weight percent NISTELLE C powder (available from the Stellite Division of Haynes International, Inc.) were rod milled to a particle size of about 1.5 microns. This powder was lubed with a pressing lubricant, then pelletized, and then sintered
25 at 2515°F for 30 minutes. The sintered product was then crushed, milled and classified to a 30x15 micron powder suitable for spray powder applications.

 Although some of the tables below reflect data for the specific composition of 80 weight percent tungsten carbide and 20 weight NISTELLE C, applicant
30 considers the scope of the invention to be broader than the 80/20 weight ratio of WC/nickel-based alloy. The tungsten carbide component may range between about 75 wt% and about 90 wt% and the nickel-based alloy
35 component may range between about 10 wt% and about 25 wt% of the spray powder.

Furthermore, applicant contemplates that other compositions of nickel-based alloys would be satisfactory to use in the present invention. These compositions include HASTELLOY C, available through
5 Haynes International, Inc., having a composition of 17 wt% Cr; 0.1 wt% C; 17 wt% Mo; 6 wt% Fe; 5 wt% W and balance Ni; HASTELLOY C, available through Teledyne
Rodney Metals, having a composition of 16-18 wt% Mo; 13-17.5 wt% Cr; 3.7-5.3 wt% W; 4.5-7 wt% Fe; and
10 balance Ni; and HASTELLOY C, available through Haynes International Inc., having a composition of 0-0.12 wt% C; 16.5 wt% Cr; 17 wt% Mo; 5.5 wt% Fe; 0-2.5 wt% Co; 4.5 wt% W; 0-1 wt% Si; 0-1 wt% Mn; and balance Ni.

15 Applicant further contemplates the use of the following nickel-based alloys: HASTELLOY B, available from Langley Alloys Ltd. or Teledyne Rodney Metals, having a composition of 26-30 wt% Mo; 4-6 wt% Fe; 0-0.12 wt% C; and 62 wt% Ni; HASTELLOY B-2, available
20 from Haynes International Inc., having a composition of 0-.01 wt% C; 26-30 wt% Mo; 0-2 wt% Fe; 0-1 wt% Cr; 0-1 wt% Mn; 0-1 wt% Co; 0-0.1 wt% Si; and the balance Ni.

Thus, the invention is of such a scope so as
25 to include a spray powder for application as a corrosion-resistant hardfacing on a substrate. The spray powder comprises between about 75 weight percent and about 90 weight percent of tungsten carbide and between about 10 weight percent and about 25 weight
30 percent of a nickel-based alloy.

In the examples, the WC is the traditional APT-based tungsten carbide; however, applicant considers the present scope of the invention to encompass WC including macrocrystalline WC. The
35 nickel-based alloy can comprise the following ranges of elements: Mo in an amount of between about 16 to about 30 weight percent of the alloy; Fe in an amount of

between about 0 to about 8 weight percent of the alloy;
C in an amount of between about 0 to about 0.12 weight
percent of the alloy; Cr in an amount of between about
0 to about 17.5 weight percent of the alloy; Mn in an
5 amount of between about 0 to about 1 weight percent of
the alloy; Co in an amount of between about 0 to about
2.5 weight percent of the alloy; Si in an amount of
between about 0 to about 1 weight percent of the alloy;
W in an amount of between 0 to about 5.3 weight percent
10 of the alloy; and nickel being the balance of the
nickel-based alloy.

EXAMPLES

The following examples demonstrate the
superior results obtained by one specific embodiment of
15 the invention as compared to the Kennametal tungsten
carbide-cobalt-chromium alloy alone. The Kennametal
tungsten carbide-cobalt-chromium alloy (which is called
WC/Co/Cr) is the sintered product from a powder mixture
of 80.8 wt% macrocrystalline tungsten carbide, 5.0 wt%
20 tungsten metal powder, 4.0 wt% chromium metal powder,
and 10.2 wt% cobalt metal powder. The chemical
properties of this alloy are:

<u>Element</u>	<u>Content (wt%) min./max.</u>
carbon	5.0/5.5
25 cobalt	9.5/10.5
chromium	3.5/4.5
iron	0.4 maximum
tungsten	balance

In order to test the corrosion resistance of
30 the hardfacing, sintered pellets of the above-discussed
specific embodiment of the invention (i.e., 80 weight
percent tungsten carbide and 20 weight percent
NISTELLE C) were tested in solutions of various
concentrations of hydrochloric acid, sulfuric acid and
35 nitric acid. The basic methodology is described below.

Sintered pellets of the specific embodiment,
having a size between about 3/8 to 1/2 inch in

diameter, were used as the samples. Each pellet was weighed, and then submerged in its respective acid solution. The solution was kept at 75°F.

At regular intervals, each pellet was removed from the solution, water washed, oven dried for one hour, and weighed before being resubmerged into the same acid solution. The results for the corrosion testing of the one specific embodiment of the invention are set forth below in Tables I through VI. Tables I, III and V show the weight of each sample taken at the start and at 5, 9, 15, 20, 26 (in Tables I and III), 33 and 40 days into the test.

Table I

Corrosion Testing by Days for 20% Alloy Powder in HCl

Sample	<u>0</u>	<u>5</u>	<u>9</u>	<u>15</u>
1	4.2555	4.2475	4.2425	4.2327
2	7.8396	7.8346	7.8290	7.8159
3	6.1194	6.1154	6.1119	6.1059
Sample	<u>20</u>	<u>26</u>	<u>33</u>	<u>40</u>
1	4.2203	4.1968	4.1616	4.1156
2	7.8013	7.7751	7.7423	7.7037
3	6.0946	6.0858	6.0763	6.0623

Note: Sample 1 was 100% HCl. Sample 2 was 50 volume % HCL. Sample 3 was 25 volume % HCl. The unit of measurement for the weight of each sample is grams.

Table II

20% Alloy in HCl

Percent Loss by Days from Original Weight

Sample	<u>0</u>	<u>5</u>	<u>9</u>	<u>15</u>
1	-	0.19%	0.31%	0.54%
2	-	0.06%	0.14%	0.30%
3	-	0.07%	0.12%	0.22%
Sample	<u>20</u>	<u>26</u>	<u>33</u>	<u>40</u>
1	0.83%	1.38%	2.21%	3.29%
2	0.49%	0.82%	1.24%	1.73%
3	0.41%	0.55%	0.70%	0.93%

Table III
Corrosion Testing by
Days for 20% Alloy Powder in H₂SO₄

	<u>Sample</u>	<u>0</u>	<u>5</u>	<u>9</u>	<u>15</u>
5	4	5.7296	5.7290	5.7278	5.7278
	5	7.1821	7.1727	7.1688	7.1650
	6	7.7931	7.7827	7.7760	7.7737
	<u>Sample</u>	<u>20</u>	<u>26</u>	<u>33</u>	<u>40</u>
10	4	5.7134	5.7126	5.7112	5.7108
	5	7.1631	7.1620	7.1608	7.1607
	6	7.7638	7.7590	7.7543	7.7522

Note: Sample 4 was 100% H₂SO₄. Sample 5 was 50% H₂SO₄. Sample 6 was 25% H₂SO₄. The unit of measurement for the weight of each sample is grams.

15

Table IV
20% Alloy in H₂SO₄ Percent
Loss by Days from Original Weight

	<u>Sample</u>	<u>0</u>	<u>5</u>	<u>9</u>	<u>15</u>
20	4	-	0.01%	0.02%	0.03%
	5	-	0.13%	0.19%	0.24%
	6	-	0.13%	0.22%	0.25%
	<u>Sample</u>	<u>20</u>	<u>26</u>	<u>33</u>	<u>40</u>
25	4	0.28%	0.30%	0.32%	0.33%
	5	0.26%	0.28%	0.30%	0.30%
	6	0.38%	0.44%	0.50%	0.52%

Table V

Corrosion Testing by
Days for 20% Alloy Powder in HNO₃

	<u>Sample</u>	<u>0</u>	<u>5</u>	<u>9</u>	<u>15</u>	<u>33</u>	<u>40</u>
30	7	6.0478	6.0478	6.0477	6.0477	6.0477	6.0477
	8	7.7395	7.7326	7.7259	7.7259	7.7259	7.7259
	9	7.1601	7.1601	7.1601	7.1601	7.1601	7.1601

Note: Sample 7 is 100% HNO₃. Sample 8 is 50% HNO₃. Sample 9 is 25% HNO₃. The unit of measurement for weight of each sample is grams.

35

Table VI
20% Alloy in HNO₃

Percent Loss by Days from Original Weight

	<u>Sample</u>	<u>0</u>	<u>5</u>	<u>9</u>	<u>15</u>	<u>33</u>	<u>40</u>
5	7		0%	0.00%	0.00%	0.00%	0.00%
	8		0.09%	0.18%	0.18%	0.18%	0.18%
	9		0.00%	0.00%	0.00%	0.00%	0.00%

As a comparison, pellets of the WC/Co/Cr spray powder (the Kennametal tungsten carbide-cobalt-chromium powder previously described) were tested at selected intervals for corrosion resistance in various concentrations of hydrochloric acid, sulfuric acid, and nitric acid. The results are set out in Tables VII to XII below. Tables VII, IX and XI show the weight of each sample at selected days into the test. Tables VIII, X and XII show the percent loss from the original weight at selected days into the test.

TABLE VII

Corrosion Testing for WC/Co/Cr In HCl

	<u>Sample</u>	<u>0</u>	<u>5</u>	<u>9</u>	<u>15</u>
20	1	3.7275	3.7163	3.7054	3.6847
	2	5.1036	5.0582	5.0435	5.0082
	3	4.7165	4.6951	4.6722	4.6334
	<u>Sample</u>	<u>20</u>	<u>26</u>	<u>40</u>	
25	1	3.6628	3.6407	3.5439	
	2	4.9633	4.9213	4.7820	
	3	4.5944	4.5552	4.4805	

Note: Sample 1 was tested in 100% HCl. Sample 2 was tested in 50% HCl. Sample 3 was tested in 25% HCl.

The unit of measurement for the weight of each sample is grams.

TABLE VIII
WC/Co/Cr in HCl Percent
Percent Loss in Days from Original Weight

	<u>Sample</u>	<u>5</u>	<u>9</u>	<u>15</u>	<u>20</u>
5	1	0.30%	0.59%	1.15%	1.74%
	2	0.89%	1.18%	1.87%	2.75%
	3	0.45%	0.94%	1.76%	2.59%
	<u>Sample</u>	<u>26</u>	<u>33</u>	<u>40</u>	
10	1	2.33%	3.84%	4.93%	
	2	3.57%	4.90%	6.30%	
	3	3.42%	4.15%	5.00%	

TABLE IX
Corrosion Testing by Days of WC/Co/Cr in H₂SO₄

	<u>Sample</u>	<u>0</u>	<u>5</u>	<u>9</u>	<u>15</u>
15	4	4.1577	4.1568	4.1566	4.1557
	5	8.8116	8.7882	8.7550	8.7206
	6	9.6663	9.5527	9.4549	9.3891
	<u>Sample</u>	<u>20</u>	<u>26</u>	<u>40</u>	
20	4	4.1544	4.1527	4.1518	
	5	8.6752	8.6304	8.6277	
	6	9.3017	9.2264	9.1722	

Note: Sample 4 was tested in 100% H₂SO₄. Sample 5 was tested in 50% H₂SO₄. Sample 6 was tested in 25% H₂SO₄. The unit of measurement for the weight of each sample is grams.

TABLE X
WC/Co/Cr in H₂SO₄ Percent
Loss by Days from Original Weight

	<u>Sample</u>	<u>0</u>	<u>5</u>	<u>9</u>	<u>15</u>
30	4	-	0.02%	0.03%	0.05%
	5	-	0.27%	0.64%	1.03%
	6	-	1.18%	2.19%	2.87%
	<u>Sample</u>	<u>20</u>	<u>26</u>	<u>33</u>	<u>40</u>
35	4	0.08%	0.12%	0.13%	0.14%
	5	1.55%	2.06%	2.07%	2.09%
	6	3.77%	4.55%	4.82%	5.11%

TABLE XI

Corrosion Testing by Days of WC/Co/Cr Alloy in HNO₃

<u>Sample</u>		<u>0</u>	<u>5</u>	<u>9</u>	<u>15</u>
5	7	3.9171	3.8767	3.8364	3.8328
	8	3.4296	3.3992	3.3696	3.3634
	9	3.4058	3.3746	3.3431	3.3425
<u>Sample</u>		<u>20</u>	<u>26</u>	<u>33</u>	<u>40</u>
10	7	3.8297	3.8254	3.821	3.8113
	8	3.3586	3.3481	3.3432	3.3325
	9	3.3421	3.3421	3.3421	3.3421

Note: Sample 7 was tested in 100% HNO₃. Sample 8 was tested in 50% HNO₃. Sample 9 was tested in 25% HNO₃. The unit of measurement for the weight of each sample is grams.

15

TABLE XII

WC/Co/Cr Alloy in HNO₃ Percent
Loss by Days from Original Weight

<u>Sample</u>		<u>0</u>	<u>5</u>	<u>9</u>	<u>15</u>
20	7	-	1.03%	2.06%	2.15%
	8	-	0.89%	1.75%	1.93%
	9	-	0.92%	1.84%	1.86%
<u>Sample</u>		<u>20</u>	<u>26</u>	<u>33</u>	<u>40</u>
25	7	2.23%	2.34%	2.45%	2.70%
	8	2.07%	2.38%	2.52%	2.83%
	9	1.87%	1.87%	1.87%	1.87%

Table XIII
Comparison of WC/Co/Cr and
Alloy of the Invention in HCl

	<u>Concentration</u>	<u>Days</u>	<u>WC/Co/Cr</u>	<u>Invention</u>
5	100%	5	.30	0.19
	100%	20	1.74	0.83
	100%	40	4.93	3.29
	50%	5	0.89	0.06
	50%	20	2.75	0.49
10	50%	40	6.30	1.73
	25	5	0.45	0.07
	25	20	2.59	0.41
	25	40	5.00	0.93

Table XIV compares the weight loss of the
15 WC/Co/Cr alloy with the invention in sulfuric acid.

Table XIV
Comparison of WC/Co/Cr Alloy
and Alloy of the Invention in H₂SO₄

	<u>Concentration</u>	<u>Days</u>	<u>WC/Co/Cr</u>	<u>Invention</u>
20	100	5	0.02	0.01
	100	20	0.08	0.28
	100	40	0.14	0.33
	50	5	0.27	0.13
	50	20	1.55	0.26
25	50	40	2.09	0.30
	25	5	1.55	0.13
	25	20	3.77	0.38
	25	40	5.11	0.52

Table XV compares the weight loss of the
30 WC/Co/Cr alloy with the invention in nitric acid.

Table XV
Comparison of WC/Co/Cr Alloy
and Alloy of the Invention in HNO₃

	<u>Concentration</u>	<u>Days</u>	<u>WC/Co/Cr</u>	<u>Invention</u>
5	100	5	1.03	0.00
	100	20	2.23	0.00
	100	40	2.70	0.00
	50	5	0.89	0.09
	50	20	2.07	0.18
10	50	40	2.83	0.18
	25	5	0.92	0.00
	25	20	1.87	0.00
	25	40	1.87	0.00

Tests were conducted to compare the abrasion-resistant properties of the invention to the Kennametal tungsten carbide-cobalt-chromium alloy. Two specific alloys of the invention were tested for abrasion resistance. One alloy comprised about 88 wt% of the traditional APT-based WC and about 12 wt% of the NISTELLE C alloy by Stellite. The other alloy comprised about 80 wt% of the traditional APT-based WC and about 20 wt% of the NISTELLE C alloy by Stellite. These tests were conducted according to ASTM B6-11 Procedure except that the test went for 50 revolutions rather than 1000 revolutions. The samples presented uniform deposits of each hardfacing with low levels of porosity. The results for the WC/Co/Cr alloy were normalized to 1.00 so that the results for the 12% alloy (88 wt% WC and 12 wt% NISTELLE C from Stellite) and 20% alloy (80 wt% WC and 20 wt% NISTELLE C from Stellite) are relative to those for the WC/Co/Cr alloy. The results are below in Table XVI.

Table XVI

	<u>Material</u>	<u>Wear</u>	<u>Hardness (R_C)</u>
35	WC/Co/Cr	1.00	44.2
	12% Alloy	.67	46.8
	20% Alloy	.65	46.4

As can be seen, each one of the specific examples has a meaningfully better abrasion resistance than the standard WC/Co/Cr alloy. Furthermore, each one of the specific examples has a greater hardness than the standard WC/Co/Cr alloy.

Samples of the 12% alloy (88 wt% WC and 12 wt% NISTELLE C) and 20% alloy (80 wt% WC and 20 wt% NISTELLE C) applied as a hardfacing to a substrate were held at a temperature of about 1000°F for 90 minutes. No significant oxidation was visible. It can thus be seen that the specific examples exhibit good resistance to oxidation at an elevated temperature.

The overall improvement in abrasion resistance and corrosion resistance displayed by the present invention over the WC/Co/Cr alloy is meaningful. However, this improvement becomes even more meaningful when viewed in light of recent hardfacing test results published by the University of Tulsa, Department of Mechanical Engineering, in Tulsa, Oklahoma, in the Fall of 1992. The particular publication is Shadley, J.R., Rybicki, E., Han, W. and Greving, D., "Evaluations of Selected Thermal Spray Coatings for Oil and Gas Industry Applications," Thermal Spray Coating Research Center, The University of Tulsa, 600 South College Avenue, Tulsa, Oklahoma 74104-3189.

The Tulsa Report reports the results of tests for erosion, abrasion, corrosion and bond strength for a number of hardfacing materials. One of the hardfacing materials is a tungsten carbide containing Co and Cr identified as Stellite JK-120. The specific composition is 86 wt% WC, 10 wt% Co and 4 wt% Cr. Although not exactly the same, the Stellite JK-120 has some similarity to the WC/Co/Cr alloy against which applicant compared the present invention. The Stellite JK-120 applied to a 1018 steel base metal via HVOF technique by Stellite Jet Kote II equipment exhibited

excellent properties in comparison to the other alloys reported in the Tulsa Report. The present invention exhibited superior corrosion-resistant and abrasion-resistant properties over the WC/Co/Cr alloy. Thus, it
5 become apparent that applicant has provided a novel spray powder alloy that has excellent abrasion-resistance and corrosion-resistance properties. The present invention also has good resistance to oxidation at elevated temperatures.

10 Other embodiments of the invention will be apparent to those skilled in the art from a consideration of the specification or practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary
15 only, with the true scope and spirit of the invention being indicated by the following claims.

-19-

WHAT IS CLAIMED IS:

1. A sintered spray powder for application as a corrosion-resistant hardfacing on a substrate, the sintered powder comprising:

5 WC in an amount between about 75 and about 90 weight percent of the sintered powder;

Mo in an amount of between about 1.6 and about 7.5 weight percent of the sintered powder;

10 Fe in an amount of between 0 and about 2 weight percent of the sintered powder;

C, other than C combined in WC, in an amount of between 0 and about 0.03 weight percent of the sintered powder;

15 Cr in an amount of between 0 and about 4.4 weight percent of the sintered powder;

Mn in an amount of between 0 and about .25 weight percent of the sintered powder;

Co in an amount of between 0 and about .63 weight percent of the sintered powder;

20 Si in an amount of between 0 and about .25 weight percent of the sintered powder;

W, other than W combined in WC, in an amount of between 0 and about 1.4 weight percent of the sintered powder; and

25 the balance nickel, wherein at least about 3.4 weight percent of the sintered powder is nickel.

2. The sintered spray powder of claim 1 wherein the Mo is present in an amount between about 2.6 and about 7.5 weight percent, the Fe is present in an amount between about .4 and about 2 weight percent, and the nickel is present in an amount between about 6.2 and about 15.5 weight percent.

3. The sintered spray powder of claim 2 wherein the Fe is present in amount between about .4 and about 1.5 weight percent.

4. The sintered spray powder of claim 1 wherein the Mo is present in an amount between about 2.6 and about 7.5 weight percent; the Fe is present in an amount between 0 and about 0.5 weight percent; the C, other than combined in the WC, is present in an amount between 0 and about 0.003 weight percent; the Cr is present in an amount between 0 and about .25 weight percent; the Co is present in an amount between 0 and about .25 weight percent; the Si is present in an amount between about 0 and about 0.025 weight percent; and the nickel is present in amount between about 6.5 and about 18.5 weight percent.

5. The sintered spray powder of claim 1 wherein the W, other than W combined in the WC, is present in an amount between about .5 and 1.25 weight percent; the Mo is present in an amount between about 1.7 and about 4.25 weight percent; the Fe is present in an amount between about .6 and 1.5 weight percent; the Cr is present in an amount between about 1.7 and about 4.25 weight percent; and Ni is present in an amount between about 5.5 weight percent and about 13.8 weight percent.

6. The sintered spray powder of claim 1 wherein the W, other than W combined in the WC, is present in an amount between about .37 and 1.4 weight percent; the Mo is present in an amount between about 1.6 and about 4.5 weight percent; the Fe is present in an amount between about .4 and about 1.43 weight

percent; the Cr is present in an amount between about 1.3 and about 4.4 weight percent; and Ni is present in an amount between about 5.3 and about 15.9 weight percent.

- 5 7. The spray powder of claim 1 wherein W, other than W combined in WC, is present in an amount between about .45 and about 1.25 weight percent; Mo is present in an amount between 1.7 and about 4.25 weight percent; Fe is present in an amount between about .55
10 and about 1.4 weight percent; Cr is present in an amount between about 1.6 to about 4.2 weight percent; Co is present in an amount between 0 and about .63 weight percent; and nickel is present in an amount between about 5.2 and about 14.1 weight percent.
- 15 8. A sintered spray powder comprising:
 about 80 weight percent of tungsten carbide;
 between about 3.2 and about 6 weight percent Mo;
20 between 0 and about 1.6 weight percent Fe;
 between 0 and about .0024 weight percent C, other than C combined in WC;
 between 0 and about 3.5 weight percent Cr;
25 between 0 and about .2 weight percent manganese;
 between 0 and about .5 weight percent cobalt;
30 between 0 and about .2 weight percent Si;
 between 0 and about 1.06 weight percent tungsten metal, other than tungsten combined in WC; and
 the balance nickel wherein at least
35 about 6.8 weight percent of the powder is nickel.

9. The spray powder of claim 8 wherein Mo in an amount of between about 3.2 and about 3.6 weight

percent; Fe in an amount of between about .8 and about 1.2 weight percent; Cr in an amount of between about 2.6 and about 3.5 weight percent; W, other than W combined in WC, in an amount of between about .74 and about 1.06 weight percent; and the balance nickel wherein at least about 10.4 weight percent of the powder is nickel.

10. A sintered spray powder comprising:
carbide;
between about 1.9 and about 3.6 weight percent Mo;
between 0 and about 1 weight percent Fe;
between 0 and about .015 weight percent C, other than C combined in WC;
between 0 and about 2.1 weight percent Cr;
between 0 and about .12 weight percent manganese;
between 0 and about .3 weight percent cobalt;
between 0 and about .12 weight percent Si;
between 0 and about .64 weight percent tungsten metal, other than tungsten combined in WC; and the balance nickel wherein at least about 4.1 weight percent of the powder is nickel.

11. The spray powder of claim 10 wherein Mo in an amount of between about 1.9 and about 2.2 weight percent; Fe in an amount of between about .48 and about .69 weight percent; Cr in an amount of between about 1.5 and about 2.1 weight percent; W, other than W combined in WC, in an amount of between about .44 and about .64 weight percent; and the balance nickel wherein at least about 6.2 weight percent of the powder is nickel.

12. A part having a surface with hardfacing on the surface, the hardfacing comprising:

WC in an amount between about 75 and about 90 weight percent;

5 Mo in an amount of between about 1.6 and about 7.5 weight percent;

Fe in an amount of between 0 and about 2 weight percent;

10 C, other than C combined in WC, in an amount of between 0 and about 0.03 weight percent;

Cr in an amount of between 0 and about 4.4 weight percent;

Mn in an amount of between 0 and about .25 weight percent;

15 Co in an amount of between 0 and about .63 weight percent;

Si in an amount of between 0 and about .25 weight percent;

20 W, other than W combined in WC, in an amount of between 0 and about 1.4 weight percent; and the balance nickel, wherein at least about 3.4 weight percent is nickel.

13. The part of claim 12 wherein in the hardfacing the Mo is present in an amount between about 2.6 and about 7.5 weight percent, the Fe is present in an amount between about .4 and about 2 weight percent, and the nickel is present in an amount between about 6.2 and about 15.5 weight percent.

14. The part of claim 13 wherein in the hardfacing the Fe is present in amount between about .4 and about 1.5 weight percent.

15. The part of claim 12 wherein in the hardfacing the Mo is present in an amount between about 2.6 and about 7.5 weight percent; the Fe is present in an amount between 0 and about 0.5 weight percent; the C, other than combined in the WC, is present in an amount between 0 and about 0.003 weight percent; the Cr

is present in an amount between 0 and about .25 weight percent; the Co is present in an amount between 0 and about .25 weight percent; the Si is present in an amount between 0 and about 0.025 weight percent; and
5 the nickel is present in amount between about 6.5 and about 18.5 weight percent.

16. The part of claim 12 wherein in the hardfacing the W, other than W combined in the WC, is present in an amount between about .5 and 1.25 weight
10 percent; the Mo is present in an amount between about 1.7 and about 4.25 weight percent; the Fe is present in an amount between about .6 and 1.5 weight percent; the Cr is present in an amount between about 1.7 and about 4.25 weight percent; and Ni is present in an amount
15 between about 5.5 weight percent and about 13.8 weight percent.

17. The part of claim 12 wherein in the hardfacing the W, other than W combined in the WC, is present in an amount between about .37 and 1.4 weight
20 percent; the Mo is present in an amount between about 1.6 and about 4.5 weight percent; the Fe is present in an amount between about .4 and about 1.43 weight percent; the Cr is present in an amount between about 1.3 and about 4.4 weight percent; and Ni is present in
25 an amount between about 5.3 and about 15.9 weight percent.

18. The part of claim 12 wherein in the hardfacing W, other than W combined in WC, is present in an amount between about .45 and about 1.25 weight
30 percent; Mo is present in an amount between 1.7 and about 4.25 weight percent; Fe is present in an amount between about .55 and about 1.4 weight percent; Cr is present in an amount between about 1.6 to about 4.2 weight percent; Co is present in an amount between
35 0 and about .63 weight percent; and nickel is present in an amount between about 5.2 and about 14.1 weight percent.

19. The part of claim 12 wherein the
hardfacing comprises: about 80 weight percent of
tungsten carbide; between about 3.2 and about 6 weight
percent Mo; between 0 and about 1.6 weight percent Fe;
5 between 0 and about .0024 weight percent C, other than
C combined in WC; between 0 and about 3.5 weight
percent Cr; between 0 and about .2 weight percent
manganese; between 0 and about .5 weight percent
cobalt; between 0 and about .2 weight percent Si;
10 between 0 and about 1.06 weight percent tungsten metal,
other than tungsten combined in WC; and the balance
nickel wherein at least about 6.8 weight percent of the
powder is nickel.

20. The part of claim 12 wherein the
15 hardfacing comprises: about 88 weight percent WC;
between about 1.9 and about 3.6 weight percent Mo;
between 0 and about 1 weight percent Fe; between 0 and
about .015 weight percent C, other than C combined in
WC; between 0 and about 2.1 weight percent Cr; between
20 0 and about .12 weight percent manganese; between 0 and
about .3 weight percent cobalt; between 0 and about
.12 weight percent Si; between 0 and about .64 weight
percent tungsten metal, other than tungsten combined in
WC; and balance nickel wherein at least about
25 4.1 /weight percent of the powder is nickel.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/01076

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :B22F 1/00, 7/06

US CL :419/14; 428/551

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 419/14; 428/551; 428/559, 552, 564; 75/236, 240, 243, 255; 419/18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

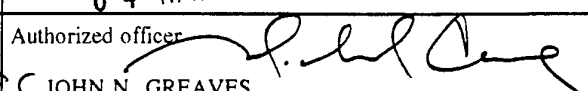
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,639,352 (KODAMA ET AL) 27 JANUARY 1987, TABLE 3	1-11
Y	US, A, 3,916,497 (DOI ET AL) 04 NOVEMBER 1975, EXAMPLES 1-11	1-11
Y	US, A, 3,878,592 (HUMENIK, JR., ET AL) 22 APRIL 1975, WHOLE DOC.	1,4,8,10,12
Y	US, A, 4,666,797 (NEWMAN ET AL) 19 MAY 1987, EXAMPLES 1-3	1-20
A	US, A, 5,057,147 (SHAFFER ET AL), 15 OCTOBER 1991	1-11

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be part of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 16 MARCH 1994	Date of mailing of the international search report 04 APR 1994
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer  JOHN N. GREAVES
Facsimile No. (703) 305-3230	Telephone No. (703) 308-0437

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/01076

(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,466,829 (NISHIGAKI ET AL) 21 AUGUST 1984	1,8,10
Y	US, A, 4,526,618 (KESHAVAN ET AL) 02 JULY 1985, COL. 2 LINES 42	1-11
A	US, A, 3,713,788 (PRILL ET AL), 30 JANUARY 1973	1-20
Y	US, A, 4,013,453 (PATEL), 22 MARCH 1977, COLS. 4-8	1-11
A	US, A, 4,923,511 (KRIZAN ET AL), 08 MAY 1990	12-20
Y	US, A, 4,446,196 (BROWN), 01 MAY 1984, CLAIMS 5 & 6	