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(54) FECRNI-STEEL ALLOYS AS CARBIDE BINDERS

(57) In the present disclosure is detailed a powder consisting by total weight of: Iron (Fe) 6.6 - 7.9 wt%, Carbon (C) 5.2 - 5.7 wt%, Chromium (Cr) 3.9 - 4.5 wt%, Nickel (Ni) 2.2 - 3.0 wt%, Molybdenum (Mo) 0.6 - 0.75 wt%, Silicon (Si) 0.1 - 0.22 wt%, Manganese (Mn) 0.07 - 0.1 wt%, the balance being tungsten (W) and unavoidable impurities, which when used in a HVOF and/or a HVAF process provides tungsten carbide embedded in a high-alloyed stainless-steel binder. As the binder is free of cobalt it provides a sustainable yet cost beneficial replacement for conventional binders for carbide products.

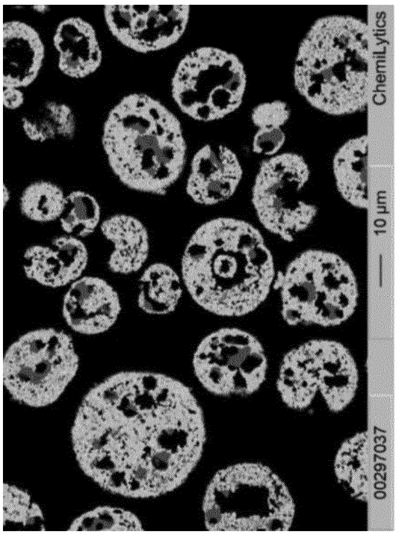

Figure 2

Processed by Luminess, 75001 PARIS (FR)

Description

TECHNICAL FIELD

[0001] In the field of powder technology for HVOF and HVAF applications there is suggested a range of stainless-steel alloys as carbide binders for, in particular, tungsten carbide.

BACKGROUND

[0002] Tungsten/chromium Carbide powders are hard materials (hardness ≈1000 HV), used for dense coatings. They can be sprayed using High-Velocity Oxygen-Fuel (HVOF) and High-Velocity Air-Fuel (HVAF) spray methods onto various metallic parts and structures to improve the surface resistance of these parts and structures to severe wear and corrosion. Conventional carbide powders consist of hard WC or Cr_3C_2 particles in a binder matrix, for which the CoCr powders are used. Different alloying elements, e.g., Ni, Fe, Ti, etc., may be added to the matrix to improve mechanical, corrosion, and spray-ability properties, c.f. e.g., J. Garcia et al. (J. Garcia, V. Collado Ciprés, A. Blomqvist and B. Kaplan, "Cemented carbide microstructures: a review," International Journal of Refractory Metals and Hard Materials, vol. 80, pp. 40-68, 2019.)

[0003] In the recent years, use of some elements, such as Co and Ni in particular, has become of concern due to their harmful characteristics to the environment and health and there have been attempts to replace these elements by less harmful elements in the binder, c.f., e.g., M. Walbrühl et al. (M Walbrühl, D. Linder, K. Ågren and A. Borgenstam, "Diffusion modeling in cemented carbides: Solubility assessment for Co, Fe and Ni binder systems," International Journal of Refractory Metals and Hard Materials, vol. 68, pp. 41-48, 2017) .

[0004] It is known that conventional binders can be replaced by high-alloyed steels, or atomized powders, c.f., e.g., J. Garcia et al. Herein, the present inventors introduce new alloys that suitable for use as a binder matrix for in particular as a binder for carbides such as tungsten carbide or diverse chromium carbides, which alloys are sustainable yet cost beneficial replacements for conventional carbide products.

[0005] These newly developed alloys are excellent candidate for coating components e.g., in aerospace or power generating technologies such as e.g., sliding tubes, sliding pistons, axles, bolts, bushings, flanges, etc. The developed alloys can also be used to coat grinding rolls, crushers, and/or calender rolls. In addition, since the alloys are Co-free materials, they can also find use in the food industry, for example for packaging rolls for plastic foils.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006]

Figure 1: Phase diagram of agglomerated/sintered carbide, made of 85% WC particles and 15% binder calculated using Thermo-Calc.
Figure 2: Cross section of agglomerated/sintered carbides, made of 85% WC particles and 15% binder.
Figure 3: Material consumption versus coverage rate for different spray techniques and parameters, as an index of efficiency and productivity.
Figure 4: Cross section of the coating achieved by JP spraying, in different magnifications. **A** scalebar 50 μm, **B** scalebar 20 μm.
Figure 5: Cross section of the coating achieved by DJ spraying, in different magnifications. **A** scalebar 50 μm, **B** scalebar 20 μm.
Figure 6: NSS tested coupons after 1008 hours for **A** JP-sprayed and **B** DJ-sprayed samples.
Figure 7: Gas permeability test results for coated samples.
Figure 8: Hardness measurements for sprayed samples using different techniques and parameters.
Figure 9: Roughness measurements for sprayed samples using different techniques and parameters.
Figure 10: Young modulus measurements for sprayed samples using different techniques and parameters.
Figure 11: Material consumption for spraying versus war resistance for sprayed samples.
Figure 12: SEM image and EDX map of elements showing different types of carbides in a Ni-rich FCC matrix.
Figure 13: Corrosion resistance measures as Cavitation index vs. material used in spraying.

[0007] It is to be understood, that the embodiments shown in the figures are for illustration of the present invention and cannot be construed as being limiting on the present invention. Unless otherwise indicated, the drawings are intended to be read (e.g., cross-hatching, arrangement of parts, proportion, degree, etc.) together with the specification, and are to be considered a portion of the entire written description of this disclosure.

DETAILED DESCRIPTION

[0008] In a first aspect and embodiment thereof, there is herein detailed an iron-chrome-nickel stainless-steel alloy consisting by total weight of the alloy of:

Chromium (Cr) :	26 - 30 wt%,
Nickel (Ni) :	15 - 18 wt%,
Molybdenum (Mo):	4 - 5 wt%,
Silicon (Si) :	1 - 1.5 wt%,
Manganese (Mn) :	0.5 - 1.0 wt%,
Carbon (C) :	0.15 - 0.25 wt%,

the balance being iron (Fe) and unavoidable impurities not exceeding 0.3 wt%.

[0009] As detailed in the below experimental section, the stainless-steel alloys of the present invention are useful as sustainable binders for carbides, such as tungsten carbide.

[0010] In embodiments of the iron-chrome-nickel stainless-steel alloy, chromium (Cr) is present from 26.5 wt%, from 27 wt%, from 27.5 wt% or from 28 wt%. In further embodiments thereof, chromium (Cr) is present to 29.5 wt%, to 28.5 wt% or to 28 wt%.

[0011] In embodiments the iron-chrome-nickel stainless-steel alloy, nickel (Ni) is present from 15.5 wt%, from 16 wt%, or from 16.5 wt%. In further embodiments thereof, nickel (Ni) is present to 17.5 wt%, to 17 wt%, or to 16.5 wt%.

[0012] In embodiments the iron-chrome-nickel stainless-steel alloy, molybdenum (Mo) is present from 4.1 wt%, from 4.25 wt%, from 4.4 wt%, or from 4.5 wt%. In further embodiments thereof, molybdenum (Mo) is present to 4.9 wt%, to 4.75 wt%, to 4.6 wt% or to 4.5 wt%.

[0013] In embodiments the iron-chrome-nickel stainless-steel alloy, silicon (Si) is present from 1.1 wt%, from 1.2 wt%, or from 1.25 wt%. In further embodiments thereof, silicon (Si) is present to 1.4 wt%, to 1.3 wt%, or to 1.25 wt%.

[0014] In embodiments the iron-chrome-nickel stainless-steel alloy, manganese (Mn) is present from 0.6 wt%, from 0.7 wt%, or from 0.75 wt%. In further embodiments thereof, manganese (Mn) is present to 0.9 wt%, to 0.8 wt% or to 0.75 wt%.

[0015] In embodiments the iron-chrome-nickel stainless-steel alloy, carbon (C) is present from 0.16 wt%, from 0.17 wt%, from 0.18 wt%, from 0.19 wt%, or from 0.20 wt%. In embodiments thereof, carbon (C) is present to 0.24 wt%, to 0.23 wt%, to 0.22 wt%, to 0.21 wt%, or to 0.20 wt%.

[0016] The alloys of the invention preferably are manufactured as powders for HVOF and/or HVAF spray coating by pre-alloying the elements of the alloy, atomizing, e.g., water-atomizing, the pre-alloyed elements, whereby a pre-alloyed stainless-steel powder containing the alloys of the invention is obtained.

[0017] In an embodiment of the pre-alloyed stainless-steel powder, the pre-alloyed stainless-steel powder comprises at least 80% by weight of the pre-alloyed stainless-steel powder contained within a sieved fraction of the pre-alloyed stainless-steel powder having a size distribution from 1 μm to 100 μm, preferably from 2.5 μm to 75 μm, or even more preferably from 5 μm to 50 μm, as measured by sieving in accordance with ISO-14232-1-2017-E, Particle distribution by sieving, and/or preferably comprises at least 85% by weight, at least 90% by weight, or more preferably at least 95% by weight of the pre-alloyed stainless-steel powder having a size distribution from 2.5 μm to 100 μm as measured by sieving in accordance with ISO-14232-1-2017-E, Particle distribution by sieving.

[0018] An advantage of the alloys of the present invention is that they can be mixed with carbides of a suitable powder size for HVOF and/or HVAF spray coating and spray coated together directly onto a suitable surface.

[0019] The benefits of the invention are exemplified herein below in the context of an agglomerated/sintered carbide product is, made from 85 wt% WC particles and 15 wt% binder. The binder and carbides are dry sprayed together and sintered at constant temperature of 1138°C for maximum two hours, thereby forming the desired tungsten carbide/stainless-steel alloy complex. Chemical composition element ranges for the forming of suitable tungsten carbide/stainless-steel alloy complexes are given in Table 1 below.

Table 1: WC/alloy complexes, Tungsten (W) balance

Element	Fe	Cr	Ni	Mo	C (total)	Si	Mn
wt%	6.6 - 7.9	3.9 - 4.5	2.2 - 3.0	0.6-0.75	5.2 - 5.7	0.1 - 0.22	0.07 - 0.1
optimal					5.3 - 5.7		

[0020] Accordingly, in a second aspect of the present invention and embodiments thereof, there is herein detailed a tungsten-based powder consisting by total weight of powder of:

Iron (Fe) :	6.6 - 7.9 wt%,
Carbon (C) :	5.2 - 5.7 wt%,
Chromium (Cr) :	3.9 - 4.5 wt%,
Nickel (Ni) :	2.2 - 3.0 wt%,
Molybdenum (Mo):	0.6 - 0.75 wt%,
Silicon (Si) :	0.1 - 0.22 wt%,
Manganese (Mn) :	0.07 - 0.1 wt%,

the balance being tungsten (W) and unavoidable impurities not exceeding 0.3 wt%.

[0021] In an embodiment of the tungsten-based powder, the amount of carbon (C) is from 5.25 to 5.7 wt%, from 5.3 to 5.7 wt%, or from 5.5 to 5.7 wt%; preferably from 5.35 to 5.7 wt%, from 5.35 to 5.65 wt%, from 5.4 to 5.65 wt%, or from 5.45 to 5.65 wt%; more preferably from 5.5 to 5.6 wt%.

[0022] In an embodiment of the tungsten-based powder, the amount of nickel (Ni) is from 2.2 to 2.7 wt%.

[0023] The tungsten-based powder can be obtained using methods otherwise known as such, e.g., by atomizing the constituting metals as a composite powder, or from a melt by partially or, preferably, fully alloying the constituting metals. In the event of the partial alloy powder or non-pre-alloyed metal powder is used, the alloying takes place during the application (e.g., spray application) of the cermet powders.

[0024] In an embodiment of the tungsten-based powder, the tungsten-based powder consists of from 13 to 17 wt% of a stainless-steel pre-alloyed powder according to the above first aspect and embodiments thereof, and from 83 to 87 wt% of a tungsten carbide (WC) powder.

[0025] In an embodiment of the tungsten-based powder, the tungsten-based powder comprises at least 80% by weight of the tungsten-based powder contained within a sieved fraction of the tungsten-based powder having a size distribution from 1 μm to 100 μm, preferably from 2.5 μm to 75 μm, or even more preferably from 5 μm to 50 μm, as measured by sieving in accordance with ISO-14232-1-2017-E, Particle distribution by sieving, and/or preferably comprises at least 85% by weight, at least 90% by weight, or more preferably at least 95% by weight of the tungsten-based powder having a size distribution from 2.5 μm to 100 μm as measured by sieving in accordance with ISO-14232-1-2017-E, Particle distribution by sieving.

[0026] In an embodiment thereof, the tungsten-based powder comprises at least 90% by weight of the tungsten-based powder contained within a sieved fraction of the tungsten-based powder having a size distribution from 5 μm to 25 μm as measured by sieving in accordance with ISO-14232-1-2017-E, Particle distribution by sieving. In preferred embodiments thereof, the tungsten-based powder comprises at least 95% by weight, at least 97% by weight, or more preferably at least 99% by weight, or even more preferably at least 99.5% by weight contained within a sieved fraction of the tungsten-based powder having a size distribution from 5 μm to 25 μm as measured by sieving in accordance with ISO-14232-1-2017-E, Particle distribution by sieving.

[0027] In an embodiment thereof, the tungsten-based powder comprises at least 90% by weight of the tungsten-based powder contained within a sieved fraction of the tungsten-based powder having a size distribution from 15 μm to 45 μm as measured by sieving in accordance with ISO-14232-1-2017-E, Particle distribution by sieving. In preferred embodiments thereof, the tungsten-based powder comprises at least 95% by weight, at least 97% by weight, or more preferably at least 99% by weight, or even more preferably at least 99.5% by weight contained within a sieved fraction of the tungsten-based powder having a size distribution from 5 μm to 25 μm as measured by sieving in accordance with ISO-14232-1-2017-E, Particle distribution by sieving.

[0028] In an aspect of the present invention, the tungsten-based powder is a cermet powder consisting of from 83 wt% to 87 wt% of the total mass of the powder provided as a pre-formed tungsten carbide (WC) powder and from 13 wt% to 17 wt% of the total mass of the powder provided as a stainless-steel pre-alloyed powder according to any aspect thereof detailed herein above.

[0029] In an embodiment thereof, the cermet powder comprises at least 80% by weight of the cermet powder contained within a sieved fraction of the cermet powder having a size distribution from 1 μm to 100 μm, preferably from 2.5 μm to 75 μm, or even more preferably from 5 μm to 50 μm, as measured by sieving in accordance with ISO-14232-1-2017-E, Particle distribution by sieving, and/or preferably comprises at least 85% by weight, at least 90% by weight, or more preferably at least 95% by weight of the cermet powder having a size distribution from 2.5 μm to 100 μm as measured by sieving in accordance with ISO-14232-1-2017-E, Particle distribution by sieving.

[0030] In an aspect of the present invention, there is herein detailed the use of a tungsten-based or a cermet powder according to any one of embodiments detailed herein for the coating of a surface by means of a thermal spray method.

[0031] Further detailed herein is a cermet formed from a tungsten-based or a cermet powder according to any one of embodiments detailed herein by means of a thermal spray method, preferably a cermet having a composition corresponding to any composition of the herein disclosed tungsten-based or cermet powders.

[0032] Further detailed herein is a shaped object having a coating with a cermet according to any embodiment of the herein detailed cermets.

[0033] Further detailed herein is a method for the production of a cermet according to any embodiment of the herein detailed cermet, or of a shaped object according to any of the herein detailed embodiments, the method having the steps:

- provision of a tungsten-based or cermet powder according to one or more of herein detailed embodiments in a form or formulation that is suitable for thermal spraying;
- carrying-out of a thermal spraying process using the powder;
- obtaining of the cermet, or of the object.

EXPERIMENTAL

[0034] Coating properties were tested for different HVOF spray parameters.

[0035] HVOF thermal spray systems use different fuels to produce coating for industrial machines' parts. The resulting coatings in general are hard, thick, and dense. In this work, two different jet guns were used for thermal spraying of the samples: Diamond jet gun (DJ), and high-pressure jet gun (JP). The fuel for the DJ consisted of O_2+H_2+air and for the JP it was a mixture of oxygen and argon.

[0036] The high-pressure jet gun (JP-5000) is designed for liquid-fuel (kerosene) and oxygen operation. Fuel and oxygen are fed into the gun, atomized by the coaxial stabilizer, and ignited in the combustion chamber, resulting in a supersonic flame. Spray powder from the powder feeder is fed radially into the supersonic flame through two powder ports positioned directly after the combustion chamber. The spray stream is accelerated through a converging/diverging nozzle several times the speed of sound. The spray particles are heated to a molten or semi-molten state and propelled at high velocity, impacting the coating surface in a plastic state. Table 2 provides an overview of the spray parameters used in the present experiments.

Table 2: Spray parameters for high-pressure jet gun (JP-5000)

Chemistry		WC-FeCrNi	WC-FeCrNi	WC-FeCrNi	WC-FeCrNi	WC-FeCrNi	WC-FeCrNi	WC-FeCrNi
Grain size [µm]		45/15	45/15	45/15	45/15	25/5	25/5	25/5
Parameter								
Nozzle	inch	4	4	6	6	4	4	4
	mm	101,6	101,6	152.4	152.4	101.6	101,6	101,6
Oxygen	nlpm	**968**	**924**	**792**	**971**	**968**	**950**	**950**
	scfh	2200	2100	1800	2208	2200	2161	2161
Fuel	lph	**22,7**	**22,7**	**22.7**	**25,3**	**22,7**	**19**	**19**
Powder feeder	g/min	**70**	**60**	**76**	**76**	**100**	**50**	**50**
Coating procedure								
Surface speed	m/min	50	50	50	50	50	50	50
Offset	mm/U	5	5	5	5	5	5	5
Spray distance	mm	380	380	380	380	380	280	250

[0037] The DiamondJet process uses oxygen, fuel gas and air to produce a high-pressure annular flame, which provides uniform heating of the axially introduced powder spray material. The gas stream is accelerated through a converging/diverging nozzle to supersonic speeds. The gas stream propels the powder particles towards the substrate. Individual particles deform plastically upon impact, tenaciously bonding the coating to the substrate. Table 3 details the spray parameters used for the present experiments.

Table 3: Spray parameters for Diamond jet gun

Grain size [µm]		45/15	25/5
Parameter			
O2	scfh	489.9	487
	nlpm	215	214
H2	scfh	1452.8	1444
	nlpm	639	635
Shroud (Air)	scfh	785.4	782
	nlpm	345	344
Powder feeder			
Feed rate	g/min	60.0	40.0
Coating procedure			
Surface speed	m/min	100	75
Offset	mm	5	4
Spray distance	mm	250	250

[0038] Different spray parameters were tested, e.g., power feeder, nozzle size, combustion pressure, etc., c.f., Tables 2 and 3. Parameters were adjusted in a way that a dense coating with optimal deposition efficiency is achieved. These parameters are general ones used and producible in any ordinary spray shop. Separate coupons were sprayed with the same parameters for different tests.

[0039] Powder sizes were determined in accordance with ISO-14232 - 1-2017-E Particle distribution by sieving and are stated as 95% of the powder mass falling inside the given size exclusion interval.

[0040] Hardness, roughness, gas permeability, Young's modulus, and wear resistance were measured for each spray parameter.

[0041] After spraying, coated samples were analyzed with optical microscope to measure the coating thickness and porosity and additionally examined using electron microscopy.

[0042] In further tests, the carbon content of samples was measured after spraying. As will be further discussed below, the content of carbon is sensitive for the herein disclosed alloys and for their suitability for use as binders as discussed herein.

[0043] Another set of coupons were placed in the natural salt spray chamber and evaluated after specific periods of time to study the corrosion properties. Corrosion resistance of the material was also evaluated based on gas permeability and cavitation tests, c.f. Figure 13.

[0044] Finally, coated samples were analyzed using SEM/EDX analysis to find a better understanding of the final product.

Calphad-based calculation

[0045] Figure 1 shows the phase diagram for the presently developed alloys as calculated using Thermo-Calc software, steel database TCFE12.

[0046] Composition range marked with green lines in the figure shows composition range of carbon content for the final carbide in wt%, which will result in cubic carbides as hard phase in an FCC matrix as binder.

[0047] Although this composition range is wider than the one suggested in table 1, carbon burn out during thermal spraying should be considered.

[0048] If the lower limit of this range is taken for the composition ($\approx$5.2 wt%), after carbon burns out, the composition will be shifted to the phase field containing M_6C, known as η-carbide which is a brittle phase with low corrosion resistance. Optimal carbon content requires a narrower window for these alloys for avoiding formation of η-carbide after spraying.

[0049] The arrow in Figure 1 shows the optimal concentration range for carbon, wherein, even after burning out, the coating's chemical composition will be as desired, when the coating takes place at about 1200°C.

Sprayed coupons

[0050] Figure 2 shows (EM) a cross section of the agglomerated/sintered carbides, wherein the product examined was made of 85% WC particles and 15% binder. Dark cubic WC carbides can be seen in a sintered binder with light color in this figure.

[0051] Sprayed coupons were cut and analyzed by a LEICA DM6 M light optical microscope, to measure the coating thickness and porosity.

[0052] Figure. 3 shows indexes correlated to deposition efficiency and coating's thickness for different spraying methods and parameters. Other products (named Amperit® 618 (WC 15FeCrAl) and 558 (WC 10Co4Cr)) are compared with this product.

[0053] Most of the trails for this product fall in the high-productivity/high-efficiency area of the plot (compatible with, and in some cases better than the existing products) which shows that this product is cost-beneficial for spraying, through which a dense coating can be achieved.

[0054] Figures 4 and 5 show cross section of the coating using JP and DJ techniques respectively. Using both techniques a dense even coating can be achieved with 0.1-0.5 % porosity, which is on par or better than what can be achieved with to existing commercial products.

[0055] The carbon content of all the samples was measured using a Leco; CS-200 / CS-600 apparatus based on non-dispersive infrared absorption after burning in an oxygen flow. Results confirm that all samples contain more than 5.3 wt% carbon and, consequently, did not suffer from carbon burnup during spraying.

Corrosion Properties

[0056] Corrosion properties of the coating were studied by natural salt spray (NSS) test using a SC1000 Weiss GmbH machines according to standard ASTM B117. Samples were placed in the chamber and inspected after specific times, i.e., after 168, 336, 504, 672, 840 and 1008 hours. Figure 6 shows the tested coupons after 1008 hours for both techniques and barely any rust on the surface can be seen on them after completion of the study period. Slight corrosion has happened in the mounting area which is expected as salt can diffuse and accumulate there.

Gas Permeability

[0057] Gas permeability test results (measured using a GPT-03 machine in accordance with standard ISO 4022) are shown in Figure 7 for the coated samples. Possibly, the gas permeability results corroborate the excellent corrosion resistance, as they show that these coatings are very dense, and that gas (and by comparison liquid salt solutions) cannot easily penetrate and attack the sample and base material even at high pressures.

Mechanical Properties

[0058] Mechanical properties of the coatings were measured. Results for hardness, roughness and Young's modulus are shown in Figures 8 to 10.

[0059] Hardness is generally an important factor when selecting between different classes of carbides. In the present work, Hardness (HV) was measured using a Struers Dura Scan machine according to standard ISO 6507,1-4:2018.

[0060] Hardnesses for tungsten carbides are generally expected to be above 1000 HV. The present product shows a general hardness of ≈1200 HV, which makes it an excellent candidate for the intended applications.

[0061] Roughness of coated samples were measured based on standards DIN EN ISO 4287 and ASME B46.1, using a MarSurf PS10 machine. The results presented in Figure 9 show an average value of 2-4 Ra for this product which is in the general accepted range for this property among different carbides (c.f., J. Garcia et al.).

[0062] Young's modulus represents elastic properties of material and is correlated to hardness. The measurements were done using a LA-wave V2-1 Fraunhofer IWS apparatus. The average value of 240-290 GPa (Figure 10) is expected for a hard material and makes it a good candidate for applications where heavy loading is applied.

[0063] Wear resistance of the coated samples was measured according to ASTM G65 (Figure 11) using a built-in machine. Volume loss is shown versus material consumption for spraying in this figure.

[0064] Figure 11 shows that all coatings show excellent wear resistance, i.e., very low volume loss for medium powder consumption in comparison with Amperit® 618 and 558. This makes the present product significantly beneficial from cost point of view and a strong candidate for application where wear properties play an important role.

SEM Analysis

[0065] A Hitachi SU6600 Scanning Electron Microscope was used to analyze coated samples. Figure 12 shows the cross section together with EDX map for high-content elements, using voltage of 15kV. The results are aligned with thermodynamic calculation, i.e., different types of carbides in a Ni-rich FCC matrix.

CLOSING COMMENTS

[0066] Although the present invention has been described in detail for purpose of illustration, it is understood that such detail is solely for that purpose, and variations can be made therein by those skilled in the art in practicing the claimed subject matter, from a study of the drawings, the disclosure, and the appended claims.

[0067] The term "comprising" as used in the claims does not exclude other elements or steps. The indefinite article "a" or "an" as used in the claims does not exclude a plurality. A unit may fulfill the functions of several means recited in the claims. A reference sign used in a claim shall not be construed as limiting the scope.

Claims

1. An iron-chrome-nickel stainless-steel alloy consisting by total weight of alloy of:

Chromium (Cr) :	26 - 30 wt%,
Nickel (Ni) :	15 - 18 wt%,
Molybdenum (Mo):	4 - 5 wt%,
Silicon (Si) :	1 - 1.5 wt%,
Manganese (Mn) :	0.5 - 1.0 wt%,
Carbon (C) :	0.15 - 0.25 wt%,

the balance being iron (Fe) and unavoidable impurities not exceeding 0.3 wt%.

2. The iron-chrome-nickel stainless-steel alloy of claim 1 as a pre-alloyed powder.

3. A pre-alloyed stainless-steel powder according to claim 2, wherein the pre-alloyed stainless-steel powder comprises at least 80% by weight of the pre-alloyed stainless-steel powder contained within a sieved fraction of the pre-alloyed stainless-steel powder having a size distribution from 1 μm to 100 μm, preferably from 2.5 μm to 75 μm, or even more preferably from 5 μm to 50 μm, as measured by sieving in accordance with ISO-14232-1-2017-E, Particle distribution by sieving, and/or preferably comprises at least 85% by weight, at least 90% by weight, or more preferably at least 95% by weight of the pre-alloyed stainless-steel powder having a size distribution from 2.5 μm to 100 μm as measured by sieving in accordance with ISO-14232-1-2017-E, Particle distribution by sieving.

4. A tungsten-based powder consisting by total weight of powder of:

Iron (Fe) :	6.6 - 7.9 wt%,
Carbon (C) :	5.2 - 5.7 wt%,
Chromium (Cr) :	3.9 - 4.5 wt%,
Nickel (Ni) :	2.2 - 3.0 wt%,
Molybdenum (Mo):	0.6 - 0.75 wt%,
Silicon (Si) :	0.1 - 0.22 wt%,
Manganese (Mn) :	0.07 - 0.1 wt%,

the balance being tungsten (W) and unavoidable impurities not exceeding 0.3 wt%.

5. A tungsten-based powder according to claim 4, wherein the amount of carbon (C) is from 5.3 to 5.7 wt%, preferably from 5.5 to 5.7 wt%.

6. A tungsten-based powder according to claim 4 or claim 5, wherein from 83 wt% to 87 wt% of the total mass of the powder is provided as a pre-formed tungsten carbide (WC) powder.

7. A tungsten-based powder according to any of the claims 4 to 6, consisting of from 13 wt% to 17 wt% of a stainless-steel pre-alloyed powder according to claim 2 or claim 3, and from 83 to 87 wt% of a tungsten carbide (WC) powder, preferably 15 wt% of a stainless-steel pre-alloyed powder according to claim 2 or claim 3, and 85 wt% of a tungsten carbide (WC) powder.

8. A tungsten-based powder according to any of the claims 4 to 7, wherein the tungsten-based powder comprises at least 80% by weight of the tungsten-based powder contained within a sieved fraction of the tungsten-based powder having a size distribution from 1 μm to 100 μm, preferably from 2.5 μm to 75 μm, or even more preferably from 5 μm to 50 μm, as measured by sieving in accordance with ISO-14232-1-2017-E, Particle distribution by sieving, and/or preferably comprises at least 85% by weight, at least 90% by weight, or more preferably at least 95% by weight of the tungsten-based powder having a size distribution from 2.5 μm to 100 μm as measured by sieving in accordance with ISO-14232-1-2017-E, Particle distribution by sieving.

9. A cermet powder consisting of from 83 wt% to 87 wt% of the total mass of the powder provided as a pre-formed tungsten carbide (WC) powder and from 13 wt% to 17 wt% of the total mass of the powder provided as a stainless-steel pre-alloyed powder according to claim 2 or claim 3.

10. A cermet powder according to claim 9, wherein the cermet powder comprises at least 80% by weight of the cermet powder contained within a sieved fraction of the cermet powder having a size distribution from 1 μm to 100 μm, preferably from 2.5 μm to 75 μm, or even more preferably from 5 μm to 50 μm, as measured by sieving in accordance with ISO-14232-1-2017-E, Particle distribution by sieving, and/or preferably comprises at least 85% by weight, at least 90% by weight, or more preferably at least 95% by weight of the cermet powder having a size distribution from 2.5 μm to 100 μm as measured by sieving in accordance with ISO-14232-1-2017-E, Particle distribution by sieving.

11. Use of the powders according to any one of claims 4 to 10 for the coating of a surface by means of a thermal spray method.

12. A cermet having a composition according to any one of claims 4 to 10.

13. A shaped object having a coating with a cermet according to claim 12.

14. A method for the production of a cermet according to claim 12 or of an object according to claim 13, having the steps:

- provision of a powder according to one or more of claims 4 to 10 in a form or formulation that is suitable for thermal spraying;
- carrying-out of a thermal spraying process using said powder;
- obtaining of said cermet or of said object.

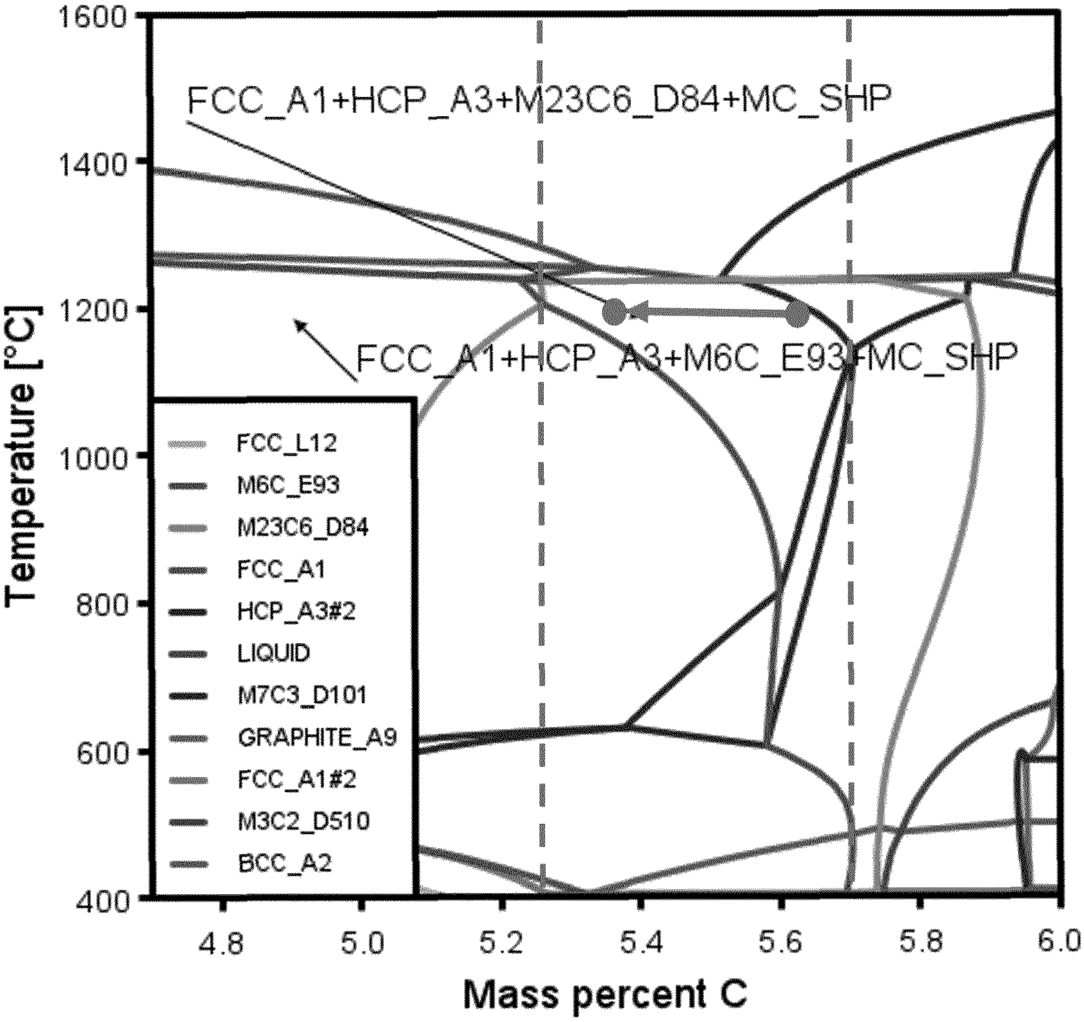
FCC_A1+HCP_A3+M23C6_D84+MC_SHP
FCC_A1+HCP_A3+M6C_E93+MC_SHP
FCC_L12
M6C_E93
M23C6_D84
FCC_A1
HCP_A3#2
LIQUID
M7C3_D101
GRAPHITE_A9
FCC_A1#2
M3C2_D510
BCC_A2
Temperature [°C]
1600
1400
1200
1000
800
600
400
4.8
5.0
5.2
5.4
5.6
5.8
6.0
Mass percent C

Figure 1

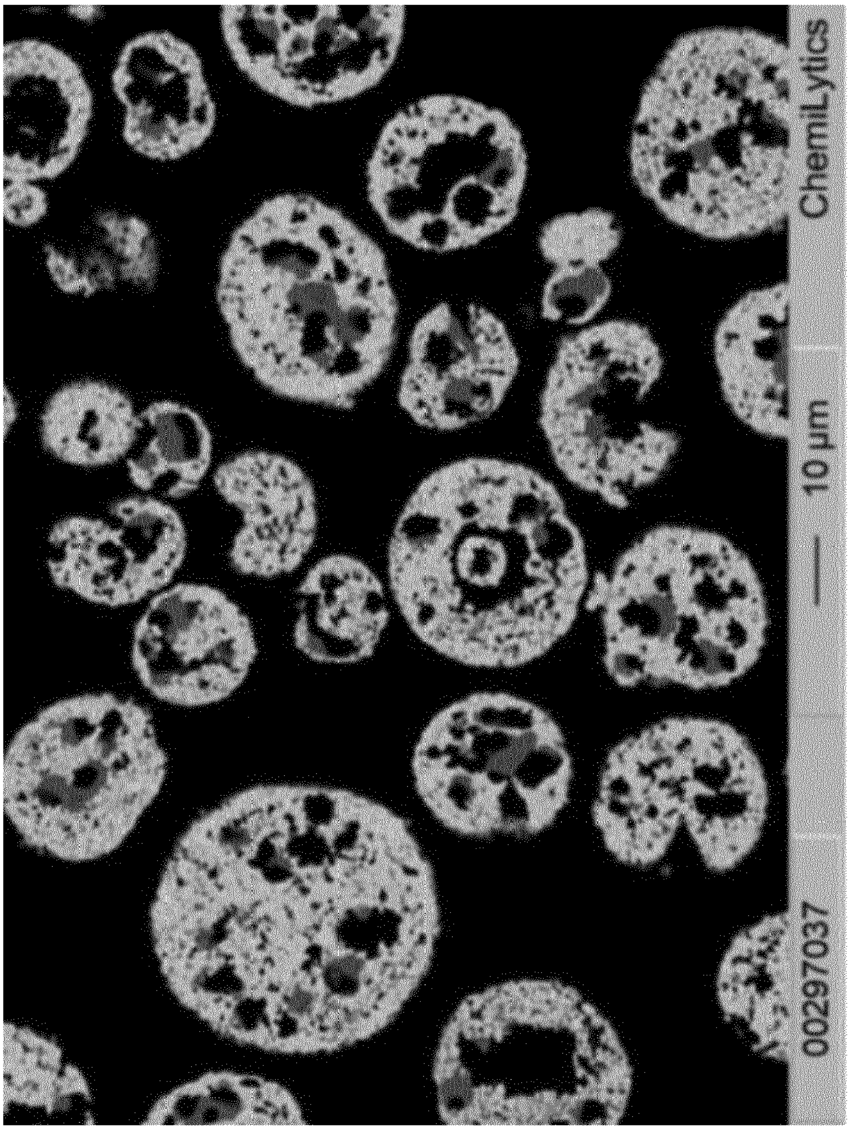

Figure 2

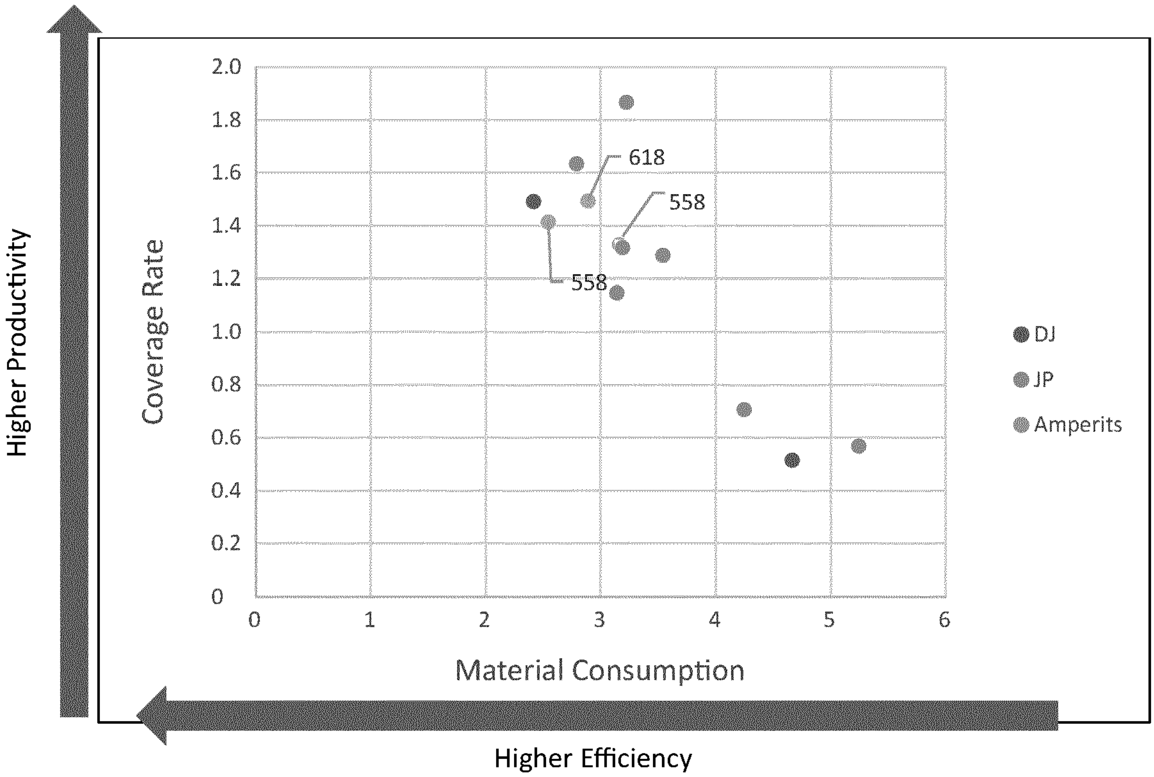
Higher Productivity
Coverage Rate
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
0
1
2
3
4
5
6
Material Consumption
618
558
558
DJ
JP
Amperits
Higher Efficiency

Figure 3

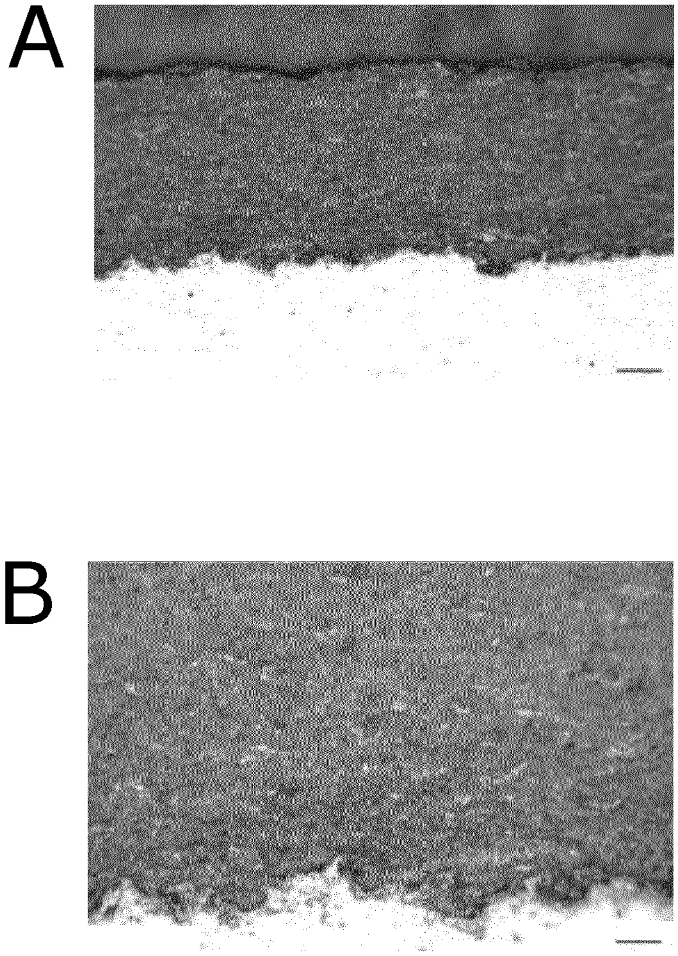

Figure 4

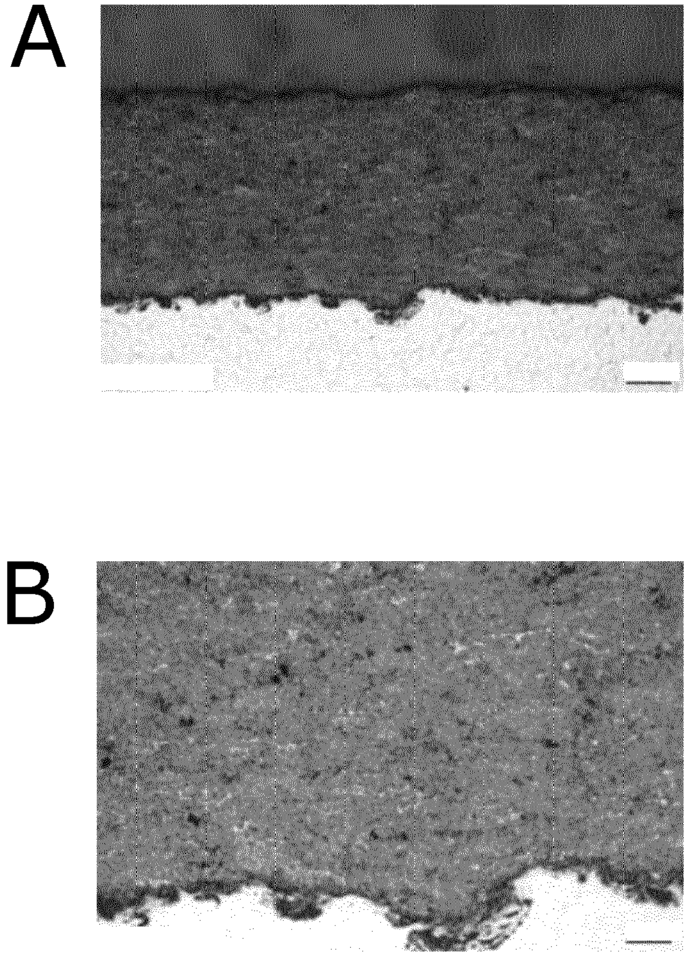

Figure 5

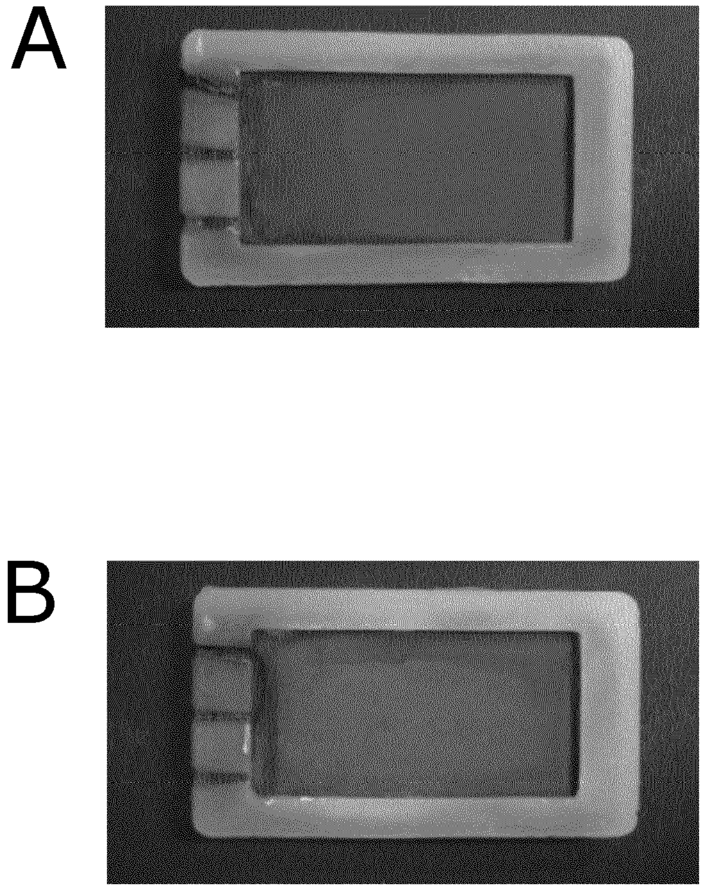

Figure 6

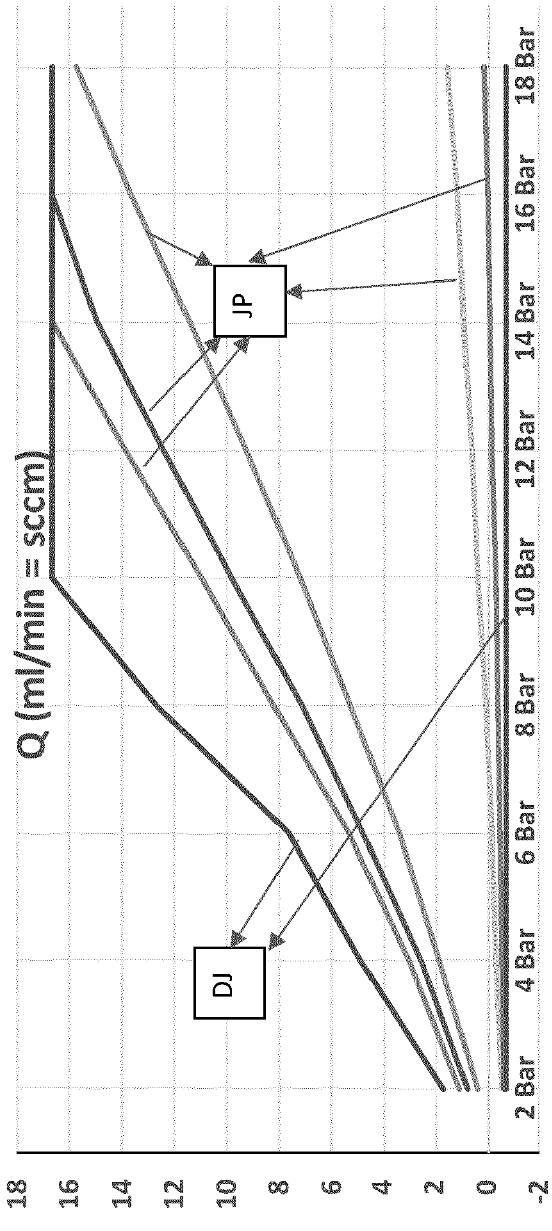
Q (ml/min = sccm)
18
16
14
12
10
8
6
4
2
0
-2
2 Bar
4 Bar
6 Bar
8 Bar
10 Bar
12 Bar
14 Bar
16 Bar
18 Bar
JP
DJ

Figure 7

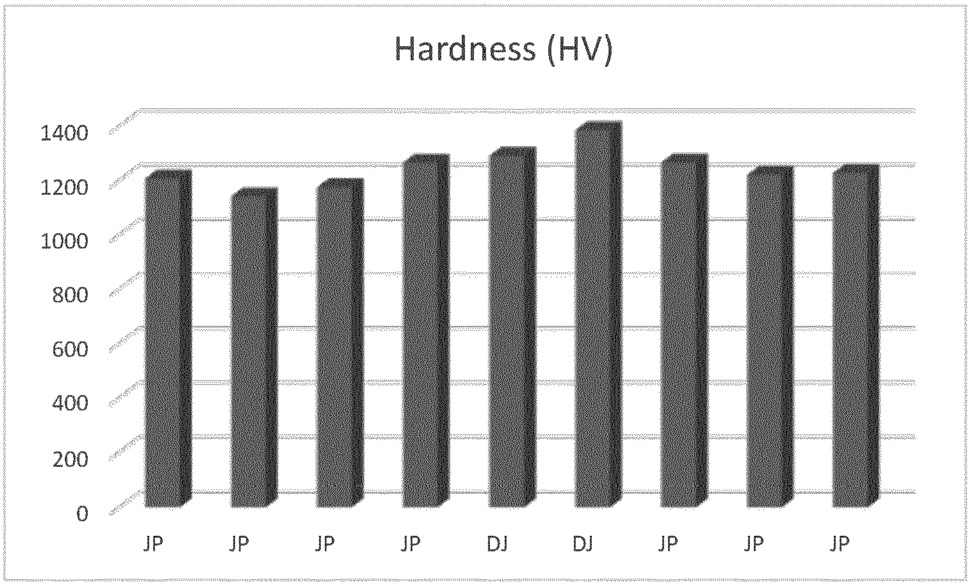
Hardness (HV)
1400
1200
1000
800
600
400
200
0
JP
JP
JP
JP
DJ
DJ
JP
JP
JP

Figure 8

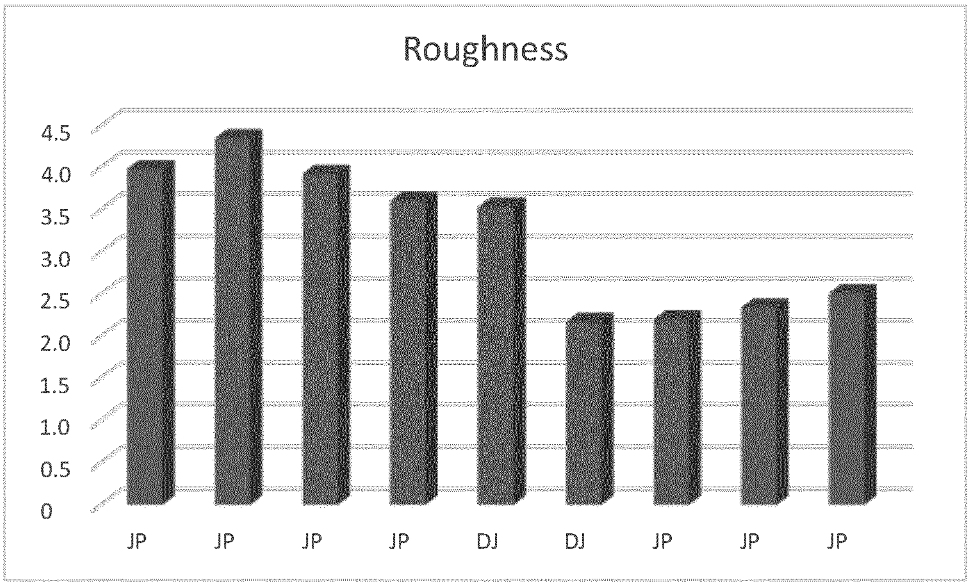

Figure 9

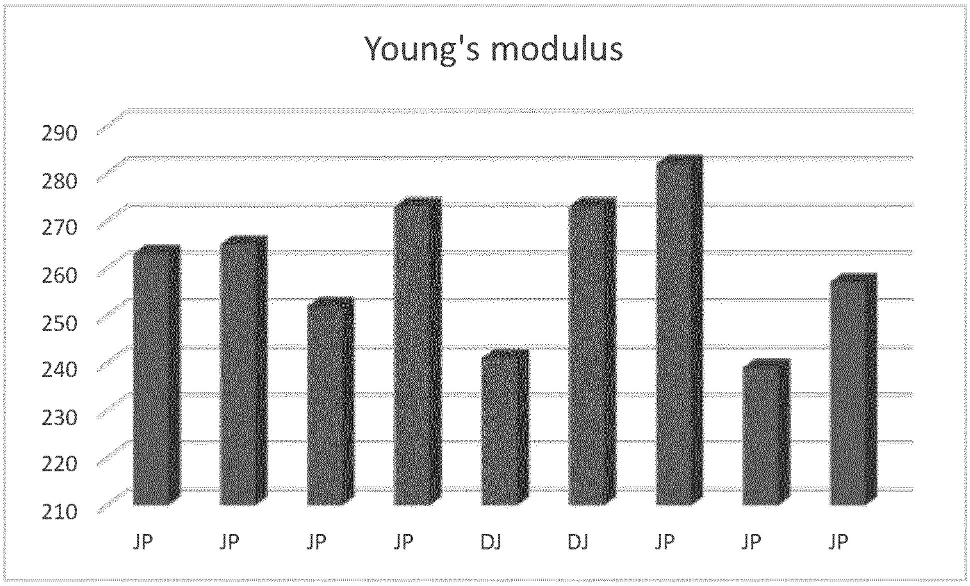
Young's modulus
290
280
270
260
250
240
230
220
210
JP
JP
JP
JP
DJ
DJ
JP
JP
JP

Figure 10

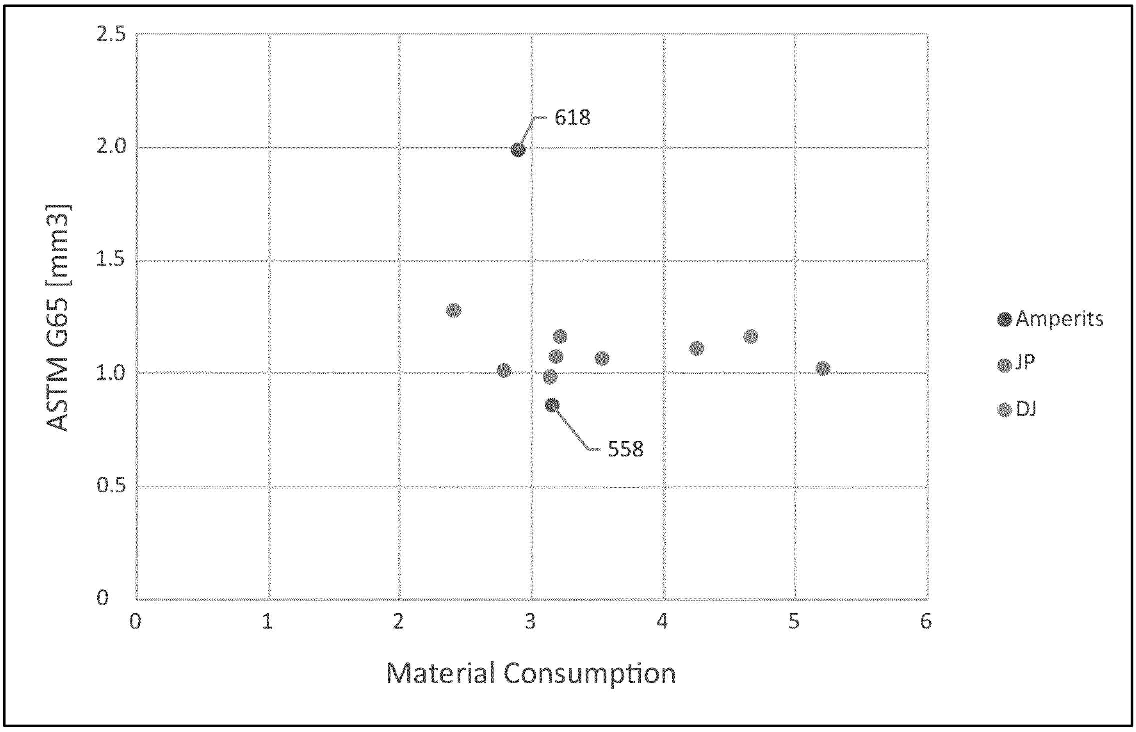
2.5
2.0
1.5
1.0
0.5
0
0
1
2
3
4
5
6
ASTM G65 [mm3]
Material Consumption
618
558
● Amperits
● JP
● DJ

Figure 11

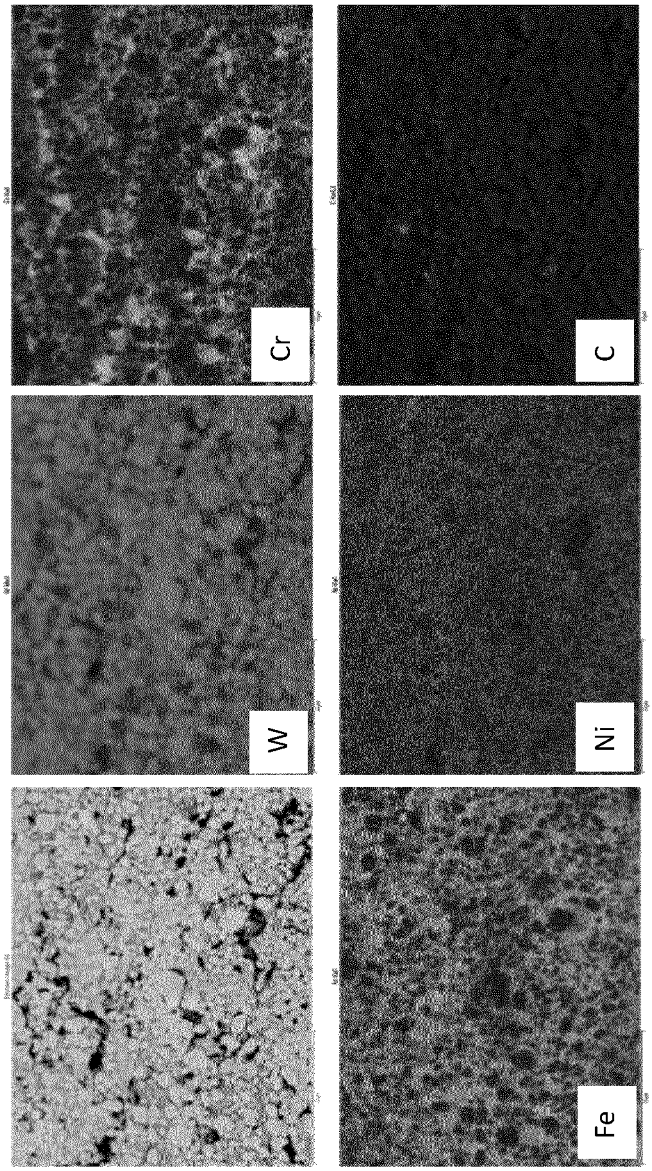

Figure 12

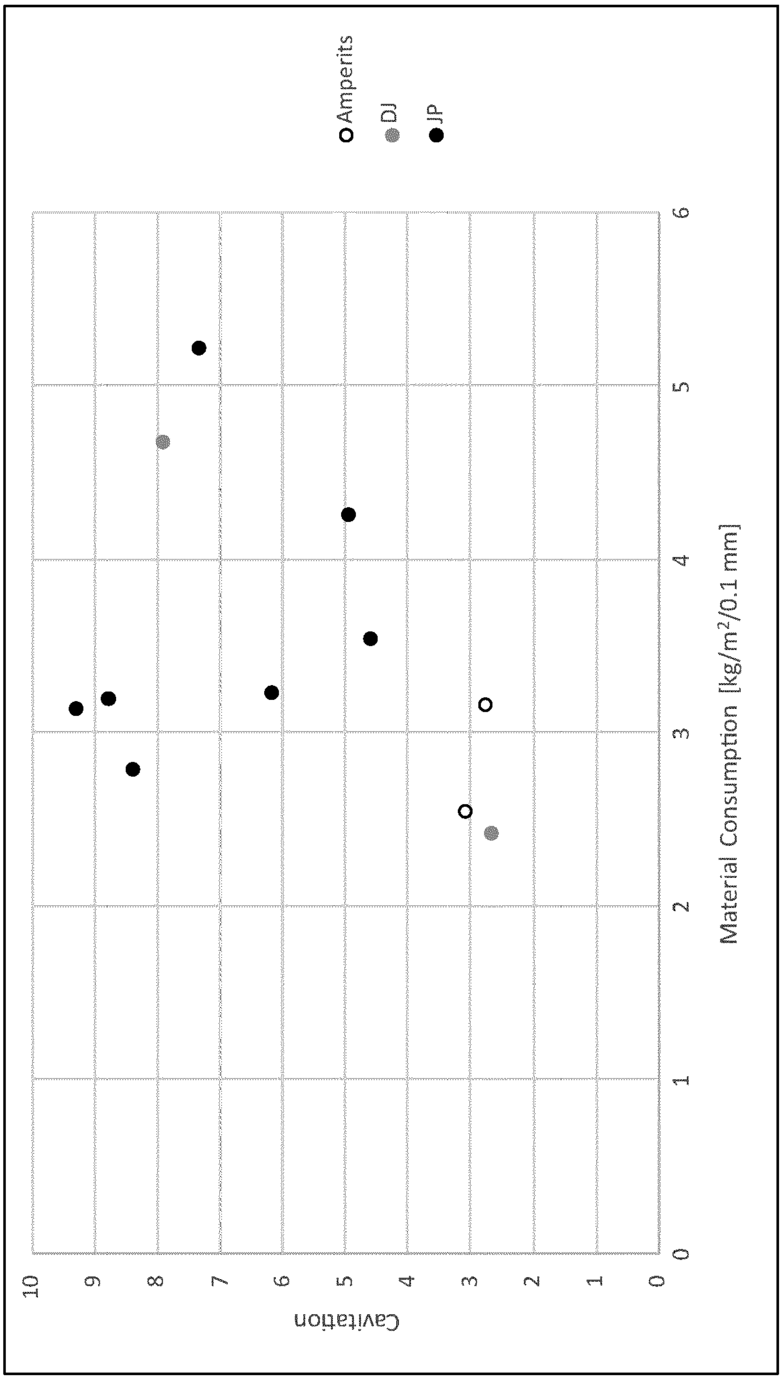
Cavitation
10
9
8
7
6
5
4
3
2
1
0
Material Consumption [kg/m^2/0.1 mm]
0
1
2
3
4
5
6
○ Amperits
● DJ
● JP

Figure 13

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 23 21 6805

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X Y	WO 2017/142430 A1 (TECH SYSTEMS FOR PROTECTIVE COATINGS LTD [RU]) 24 August 2017 (2017-08-24) * paragraphs [0031], [0038], [0041] *	1-3 4-14	INV. C22C33/02 C22C38/02 C22C38/04 C22C38/08 C22C38/22 C22C29/06 C22C29/08 C22C38/44 ADD. C22C38/00
Y	US 2014/234548 A1 (ZIMMERMANN STEFAN [DE] ET AL) 21 August 2014 (2014-08-21) * No.5; table 1 * * paragraphs [0054], [0071], [0072] *	4-14	
			TECHNICAL FIELDS SEARCHED (IPC)
			C22C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	2 May 2024	Forestier, Gilles

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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P : intermediate document

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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
&: member of the same patent family, corresponding document

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EP 23 21 6805

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02-05-2024

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2017142430 A1	24-08-2017	RU 2016104928 A	21-08-2017
		WO 2017142430 A1	24-08-2017
US 2014234548 A1	21-08-2014	AU 2012306492 A1	13-03-2014
		CA 2845506 A1	14-03-2013
		CN 103781929 A	07-05-2014
		DE 102011112435 B3	25-10-2012
		EP 2753722 A1	16-07-2014
		JP 6116569 B2	19-04-2017
		JP 2014531509 A	27-11-2014
		KR 20140058673 A	14-05-2014
		MX 359657 B	05-10-2018
		RU 2014113180 A	20-10-2015
		US 2014234548 A1	21-08-2014
		WO 2013034544 A1	14-03-2013

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

Non-patent literature cited in the description

- **J. GARCIA** ; **V. COLLADO CIPRÉS** ; **A. BLOMQVIST** ; **B. KAPLAN**. Cemented carbide microstructures: a review. *International Journal of Refractory Metals and Hard Materials*, 2019, vol. 80, 40-68 **[0002]**
- **M WALBRÜHL** ; **D. LINDER** ; **K. ÅGREN** ; **A. BORGENSTAM**. Diffusion modeling in cemented carbides: Solubility assessment for Co, Fe and Ni binder systems. *International Journal of Refractory Metals and Hard Materials*, 2017, vol. 68, 41-48 **[0003]**