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(54) **TUNGSTEN CARBIDE AND TITANIUM CARBIDE REINFORCED MANGANESE STEEL**

(57) A composite material comprising: at least one reinforcing zone comprising tungsten carbide (WC) and titanium carbide (W, Ti)C and a manganese steel matrix; a manganese steel zone that surrounds each of the reinforcing zones; and an interface layer positioned between each of the reinforcing zones and the manganese steel zone characterized in that: the average grain size of the (W, Ti)C particles in each of the reinforcing zone(s) is between 0.2-2 μm and the average grains size of the WC particles in each of the reinforcing zone(s) is between 20 - 30 μm.

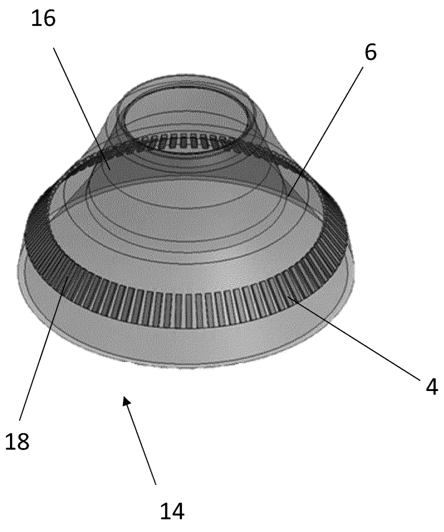

Fig. 5

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Description

TECHNICAL FIELD

[0001] The present invention relates to a composite material based on reinforced manganese steel, a wear part made thereof and a method for making the same.

BACKGROUND

[0002] A particular category of wear resistant steels are typically referred to as manganese steel or Hatfield steel. These materials are suitable for applications where a high toughness and a moderate abrasion resistance are required including for example use as wear parts for crushers that are subjected to strong abrasion and dynamic surface pressures due to the rock crushing action. Abrasion results when the rock material contacts the wear part and strips-off material from the wear part surface. Additionally, the surface of the wear part is subjected to significantly high surface pressures that cause wear part fatigue and breakage.

[0003] Manganese or Hadfield steel is typically characterised by having an amount of manganese, usually above 11% by weight. However, the problem with manganese steel is that it is typically too ductile for wear parts in modern crushers that are subject to extreme operating conditions, meaning the at the lifetime of the wear parts is reduced and the maintenance costs are increased. Therefore, the problem to be solved is to provide a manganese steel with enhanced wear resistance.

[0004] A known solution is to reinforce at least part of the manganese steel with particles having an increased hardness. WO20200222662 discloses a composite material, however the problem with this material is that is not provide an optimal balance between wear resistance and impact resistance and an even more significant problem is that there is poor bonding between the reinforcing particle and the manganese steel matrix and poor bonding between reinforced and non-reinforced zones, which leads reduced wear resistance and premature failure of the wear parts.

[0005] Therefore, the problem to be solved is to provide a composite material that can be used for wear parts having an optimal balance between wear resistance and impact resistance, wherein there is improved bonding between the reinforcing particles and the manganese matrix and the bonding between the reinforced and non-reinforced zones in order to reduce defects and cracking that would lead to premature failure of the wear parts.

DEFINITIONS

[0006] A "catalysis" is a metal powder or mixture of metal powders which during the reaction in the self-propagating high temperature synthesis (SHS) undergo melting and form a matrix of the composite zone. The fundamental role of catalysis is to reduce the amount of dissipated energy in the SHS process.

[0007] A "compact" is a densified powder composition.

SUMMARY OF INVENTION

[0008] It is an objective of this invention to provide a novel and improved composite material for wear parts. The objective is achieved by providing a composite material comprising: at least one reinforcing zone comprising core-rim tungsten titanium carbide (W,Ti)C, tungsten (WC) and a manganese steel matrix; a manganese steel zone that surrounds each of the reinforcing zones; and an interface layer positioned between each of the reinforcing zones and the manganese steel zone; characterized in that: the average grain size of the (W,Ti)C particles in each of the reinforcing zone(s) is between 0.2-2 μm, preferably between 1-2 μm and the WC particles in each of the reinforcing zone(s) is between 20-30 μm, preferably between 20-25 μm.

[0009] Advantageously, this produces a composite material that has both increased wear resistance and structural integrity. Therefore, when the material is used on areas of wear parts that are highly exposed to wear the lifetime of the parts is increased. If the average grain size of the (W,Ti)C and WC grains is too large, then the composite material will be too brittle. If the average grain size of the (W,Ti)C and WC grains in too small the wear resistance will be reduced.

[0010] Preferably, the composite material comprises between 80-98 wt% of (W,Ti)C and between 0-30% WC in each of the reinforcing zones. Preferably between 90-98 wt% of (W,Ti) C and 20-30% of WC respectively, even more preferably between 94-98 wt% and 25-30% of (W,Ti)C and WC respectively. Advantageously, this provides the optimal balance between wear resistance and impact resistance. If the wt% of (W,Ti)C and WC in each of the reinforcing zones in too high the composite material will be too brittle and more prone to failure. If the wt% of the (W,Ti)C and WC in each of the reinforcing zones is too low, then composite material will have low hardness and therefore it will not have sufficient wear resistance.

[0011] Preferably, the composition of the manganese steel in manganese steel zone has the chemical composition by weight of: carbon: 0.5 to 2.0%; manganese: 11 to 22%; silicon: 0.2 to 1.0%; chromium: 1 to 2%; nickel: up to 0.6%; molybdenum: up to 0.5%; and a balance of Iron. Advantageously, this steel composition is characterized by the addition of micro-alloying elements such as chromium, nickel and molybdenum in good amounts which induce high yield strength and high hardness resulting in increase in wear resistance of manganese steel.

[0012] Preferably, the Vickers hardness of the reinforcing zones is between 900-1400 HV1 and the hardness of the manganese steel zone is between 300 - 400 HV1 before work hardening. Advantageously, the increased hardness in the reinforcing zones leads to a more wear resistant material.

[0013] Preferably, the thickness of each of the interface layer is greater than 150 μm, preferably greater than 100 μm, even more preferably greater than 90 μm. Advantageously, this thickness of interface layer or thickness of contact area between manganese and composite zone is an indication of an increase in the reaction propagation rate and the amount of heat generated due to the high combustion temperature taking place at the contact between the molten Manganese steel and the insert. If the thickness is too large the heat conductivity increases in the composite zone which results in a faster heat dissipation towards the inside of the composite zone resulting in high nucleation rate of (W,Ti)C and WC particles. If the thickness is too small the heat conductivity is less which favours growth, consequently less nucleation of (W,Ti)C and WC particles.

[0014] Preferably, the interface layer is free of defects. Advantageously, the absence of any defects in the interface layer means that there is good bonding between the manganese steel zone and each of the reinforcing zones and consequently the structural integrity of the composite material is improved, meaning that the lifetime of the wear parts that the materials is used in is increased. Further, the absence of the presence of any pores is an indication that the composition has the ability to absorb the excess heat and gases from the SHS process and so therefore signifies that the synthesis reaction has been successful.

[0015] Preferably, the wettability between the (W,Ti)C and WC grains and the manganese steel in the reinforcing zone (s) is >99%, preferably >99.5%, even more preferably >99.9%. Advantageously, good wettability induces an excellent bonding between the composite zone and Manganese steel preventing defects such as pores and cracks to form and consequently the wear resistance increases.

[0016] Preferably, the each of the reinforcing zones has a volume of between 30-75 cm^3. Advantageously, this size provides the optimal balance between wear resistance and impact resistance.

[0017] Preferably, at least 90 %, more preferably at least 95% of the (W,Ti)C have a core-rim structure which has a rounded shape with a gradient of compositions from the centre to the outside of the particles where the core is rich in Ti and the shell is rich with W. WC grains in the reinforcing zones have an irregular prismatic shapes including triangular to rectangular shapes. Advantageously, the core-rim structure with a round shape of (W,Ti)C and the different prismatic shapes of WC will contribute to crack deflection and stop crack propagation increasing the ductility and high wear resistance of the reinforcing zone. Advantageously, the prismatic shapes of WC of will contribute to crack deflection and stop crack propagation increasing the ductility and high wear resistance of the reinforcing zone. Meanwhile, the core-rim shape will help to reduce the stress concentration under load.

[0018] Preferably, the distance between two neighbouring reinforcing zones is between 0.5 to 50 μm, preferably between 0.5-10 μm, more preferably between 0.5-5 μm. Advantageously, this provides the optimal balance between wear resistance and impact resistance. If the reinforcing zones are spaced too far apart then the wear resistance will not be high enough. If the reinforcing zones are spaced to close together then the impact resistance will not be high enough.

[0019] Another aspect of the present invention relates to a wear part comprising the composite material as described hereinbefore or hereinafter. Advantageously, the presence of the reinforcing zones within the manganese zone will improve the wear resistance and therefore the lifetime of the wear parts which in turn increases profitability.

[0020] Another aspect of the present invention relates to a method of producing the composite material as described hereinbefore or hereinafter comprising the steps of: a) mixing together 65-98 wt% tungsten, 3-90 wt% titanium, 3-20wt% carbon and 0-80 % catalysis powder; b) compacting the mixed powders together to form at least one compact; c) positioning and optionally fixing at least one compact into the interior of a mold; d) pouring molten casting manganese steel into the mold to surround the at least one compact to initiate a self-propagating high temperature synthesis (SHS) reaction to produce a cast; e) heat treating the cast; f) quenching the cast; wherein: in step b) the powders are compacting with a pressure of between 400-700 MPa, preferably between 500-600 MPa, more preferably between 550-600 MPa.

[0021] Advantageously, if this pressing pressure is used the compacts have a low density which enables the manganese steel to more easily infiltrate between the WC and TiC grains and consequently results in improved bonding between the WC and TiC grains and the manganese steel. Further it avoids the creation of defects which would lead to premature failure of the wear parts that the composite material is used in.

[0022] Preferably, the catalysis is selected from Fe, Mn, Ni, Mo, Cr, W, Al, or a mixture thereof. Advantageously, the addition of a catalysis in a specific amount will contribute to a strong stabilization to austenite phase within the microstructure in addition to good mechanical properties and high wear resistance. The catalysis addition will also act as a grain growth inhibitor which results in a fine microstructure.

BRIEF DECRSIPTION OF DRAWINGS

[0023]

Figure 1: Shows a line drawing of the composition of the composite material.

Figure 2: Shows an SEM image taken of the reinforced zone with low magnification on the left and high magnification on the right.

Figure 3: Shows an SEM image taken of the interface layer with low magnification on the left and high magnification on the right.

Figure 4: Shows an SEM image of the composite material

Figure 5: Shows a perspective drawing of a wear part.

Figure 6: Shows defects in sample E

DETAILED DESCRIPTION

[0024] Figure 1 shows a composite material 2 comprising at least one reinforcing zone 4 comprising tungsten carbide (W,Ti)C and tungsten carbide (WC) and a manganese steel matrix; a manganese steel zone 6 that surrounds each of the reinforcing zones 4 ; and an interface layer 8 positioned between each of the reinforcing zones 4 and the manganese steel zone 6. In each of the reinforcing zones, the (W,Ti)C and WC acts to reinforce the manganese steel matrix.

[0025] The average grain size of the (W,Ti)C particles in each of the reinforcing zone(s) (4) is between 0.2-2 μm, preferably between 1-2 μm. The average grain size of the WC particles in each of the reinforcing zone(s) (4) is between 20-30 μm, preferably between 20-25 μm.

[0026] The average grain size of the (W,Ti)C and WC grains is measured by Scanning Electron Microscopy (SEM) analysis where several and different areas from the samples were analysed and particle sizes were measured using Image J software. Then, the average particle size was calculated.

[0027] Each interface layer 8 comprises (W,Ti)C, WC and manganese steel and can be distinguished from the reinforcing zones 4 as the shape and size of the (W,Ti)C and WC grains are different. The interface layer(s) 8 can be distinguished from the reinforcing zone(s) 4 can either: comparing the geometry and / or comparing the average grain size. If the geometry is being compared, the reinforcing zone(s) 4 comprise >90% WC grains having irregular prismatic geometry whereas the interface layer(s) 8 comprise <5% WC grains having rectangular prismatic geometry. A WC grain is considered to have rectangular prismatic geometry if the grains have 4 sharp edges. A (W,Ti)C is considered to have a core-rim structure with a round geometry if it has a dark colour core (rich in Ti) and light colour shell (rich in W). If the grain size is being compared the average WC grain size of in the interface layer(s) 8 is at least 5% less than the average WC grain size on the reinforcing zone(s) 4.

[0028] Figure 2 shows a Scanning Electron microscope image using MIRA3 TESCAN equipment. A secondary electron detector (SE) with a high voltage of 15 KV and a working distance of 9 mm configuration were used. SEM image of the (W,Ti)C and WC grains in the reinforcing zone 4. Figure 3 shows an SEM image of the (W,Ti)C and WC grains in the interface layer 8. The different (W,Ti)C and WC grain geometry and size can clearly be seen when comparing these two figures.

[0029] In one embodiment the wt% of (W,TiC) in each of the reinforcing zones 4 is between 80-98 %, more preferably between 90-98 %, even more preferably between 94-98% and the wt% of WC in each of the reinforcing zones 4 is between 0-30 %, more preferably between 20-30 %, even more preferably between 25-30%.

[0030] In one embodiment, the composition of the manganese steel in manganese steel zone 6 has the chemical composition by weight of: carbon: 0.5 to 2.0%; manganese: 11 to 22%; silicon: 0.2 to 1.0% ; chromium: 1 to 2%; nickel: up to 0.6%, molybdenum: up to 0.5% and a balance of Fe.

[0031] In one embodiment, the chemical composition of the manganese steel in each of the reinforcing zones 4 has the chemical composition by weight of: 1-1.5 %C, 11-14 % Mn, 0.4-0.8 % Si, 1.3-2.0 % Cr, 0.6 % Ni, 0.065 % P.

[0032] In one embodiment, the hardness of the reinforcing zones 4 is between 900-1400 HV1, preferably between 1000-1400. The hardness of the manganese steel zone 6 is between 300-400 HV1.

[0033] Hardness is measured using Vickers hardness mapping on polished samples using a 1 kgf and a holding time of 15 seconds. A micro-hardness tester, Matsuzawa, model MXT was used. Hardness measurement profiles are performed starting from the non-reinforce zone, moving to the interface layer and then to the reinforced zone.

[0034] In one embodiment, the interface layer 6 is greater than 150 um wide, preferably greater than 100 μm. Figure

4 shows an SEM image taken at 15.0kV, 219 magnification of the reinforced zone 4, the manganese steel zone 6 and the interface layer 8. The width of the interface layer 6 is measured from a start point 10, which is defined as being adjacent to the manganese steel zone 6 and the point at where the (W,Ti)C and WC grains are present. The end point 12 for measuring where the interface layer 8 ends, and therefore where the reinforcing zone 8 starts is considered to be where the average grain size of the WC grains has increased by 20% compared average WC grains measured at the start point 10 and / or where the percentage of WC grains having a triangular prismatic shape increases above 90%.

[0035] In one embodiment, the interface layer 8 is free of defects. Defects are considered to be cracks or pores.

[0036] In one embodiment, the wettability between the (W,Ti)C grains and the manganese steel and between the WC and the manganese steel in the reinforcing zones 4 is >99%, preferably >99.5%, more preferably >99.9%, most preferably 100%. Wettability is measured by a Scanning Electron Microscope where the contact area and the bonding between the (W,Ti)C grains or WC grains and the manganese steel have been evaluated.

[0037] In one embodiment each of the reinforcing zones 4 has a volume of between 30-75 cm^3. For example, but not limited to the reinforcing zone(s) 4 could have a length of between 100-200 mm, preferably between 100-150 mm, a width of between 20-30 mm, preferably between 20-25 mm and a thickness between 15-30 mm, preferably between 15-25 mm.

[0038] In one embodiment >95%, preferably >98%, more preferably >99% of the (W,Ti)C grains in the reinforcing zones 4 have a rounded shape. Preferably, the (W,Ti)C grains are uniformly distributed in the manganese steel in the reinforcing zone(s). In one embodiment >95%, preferably >98%, more preferably >99% of the WC grains in the reinforcing zones 4 have a triangular prismatic shape. Preferably, the TiC grains are uniformly distributed in the manganese steel in the reinforcing zone(s).

[0039] In one embodiment, there are a plurality of reinforcing zones 4 with its interface zone 8 and the distance between two neighbouring reinforcing zones 4 with its interface layer 8 is between 1-5 mm, preferably between 1-3 mm, more preferably between 1-2 mm.

[0040] Figure 5 shows an example of a wear part 14 comprising the composite material 2 as described hereinabove or hereinafter. For example, the wear part 2 could be, but not limited to, a cone crusher or a stationary jaw crusher or a mobile jaw crusher that is configured to crush material or other material/rock processing unit. The reinforcing zone(s) 4 are positions on the wear parts 14 in the locations that are most subjected to high wear, for example on a crushing zone 18 of a cone crusher 16.

[0041] The method for producing the composite material 2 as described hereinbefore or hereinafter comprising the steps of: a) Mixing together 65-98 wt% tungsten, preferably 80-98 wt% tungsten; 3-90 wt%, preferably 10-90 wt% TiC; 3-20 wt%, preferably 3-20% carbon and 0-80 %, preferably 10-20 % catalysis powders; b) compacting the mixed powders together to form at least one compact using a compacting pressure of between 400-700MPa, preferably 500-600 MPa more preferably 550-600 MPa; c) positioning and optionally fixing at least one compact into the interior of a mold; d) pouring molten casting manganese steel into the mold to surround the at least one compact to initiate a self-propagating high temperature synthesis (SHS) reaction to produce a cast; e) heat treating the cast; and then f) quenching the cast.

[0042] Preferably, the cast is treated at a temperature of between 1400-1500°C, the cast is quenched using water. Preferably, the catalysis is selected from Fe, Co, Ni, Mo, Cr, W, Al, or a mixture thereof. Carbon could be added in the form of graphite, amorphous graphite, a carbonaceous material or mixtures thereof. The compacts could for example be held in place using me a metallic fixation system to hold them in place during casting.

EXAMPLES

Example 1 - Samples

[0043] Sample A is a comparative sample of non-reinforced manganese steel having the composition 1-1.5 %C, 11-14 % Mn, 0.4-0.8 % Si, 1.3-2.0 % Cr, 0.6 % Ni, 0.065 % P.

[0044] Samples A-I are samples of composite materials produced by mixing together powders of tungsten, titanium, carbon and a catalysis powder. The compacting the mixed powders to form compacts which were then positioned in a mold and then molten manganese steel having a composition of 1-1.5 %C, 11-14 % Mn, 0.4-0.8 % Si, 1.3-2.0 % Cr, 0.6 % Ni, 0.065 % was poured into the mold to surround the compacts which initiated a SHS reaction, the cast was then heat treated at a temperature of 1450 °C and then quenching with water. Table 1 shows a summary of the reinforced samples:

Table 1: Summary of samples

Sample	Compacting pressure used (mPA)	Average (W,Ti)C grain size in reinforcing zone (μm)	(W,Ti)C content in reinforced zone (wt%)	Average WC grain size in reinforcing zone (μm)	WC content in reinforcing zone (wt%)	Wettability (%)
A (inventive)	600	1.88	98	-	0	100
B (inventive)	600	1.04	90	20	10	100
C (inventive)	600	0.95	94	25	30	100
D (inventive)	600	0.82	98	-	0	100
E (comparative)	600	0.49	80 (pores)	-	0	80
F (inventive)	600	0.36	98	25	30	100
G (inventive)	600	0.74	98	25	20	100
H (inventive)	600	1.27	98	25	30	100
I (inventive)	600	1.04	98	25	25	100

[0045] It can be seen if the compacting pressure is not high enough then the wettability is reduced.

Example 2 - Hardness

[0046] Vickers hardness was measured by a micro-hardness tester, Matsuzawa, model MXT using 1 kgf and a holding time of 15 seconds. Hardness measurement profiles are performed starting from the non-reinforce zone, moving to the interface layer and then to the reinforced zone.

[0047] The hardness measurement results are shown in Table 2 below:

Table 2: Hardness measurement

Sample	Hardness in manganese steel zone (HV1)	Hardness in Interface layer	Hardness in reinforced zone
A (inventive)	582±36	956±90	1267±227
B (inventive)	460±62	937±85	1111±165
C (inventive)	469±37	970±82	1067±172
D (inventive)	487±32	920±67	1120±277
E (comparative)	-	-	
F (inventive)	552±53	950±81	1148±153
G (inventive)	450±50	886±19	1030±147
H (inventive)	472±119	876±86	1062±187
I(inventive)	621±37	926±30	1030±141

[0048] It can be seen that the inventive samples have an increased hardness in reinforced zones compared to the comparative samples. It was not possible to measure the hardness of E due to the large size of the pores.

Example 3 - Defects

[0049]

Table 4: Defects

Sample	Defects in the reinforced zone	Defects in the interface layer
A (inventive)	Small pores	none
B (inventive)	Small pores	none
C (inventive)	Small Pores	none
D (inventive)	Small Pores	none
E (comparative)	Big pores and cracks	Big pores and cracks
F (inventive)	Small Pores	none
G (inventive)	Small Pores	none
H (inventive)	Small Pores	none
I (inventive)	Small Pores	none

[0050] Defects were assessed by using Scanning Electron microscopy analysis where cracks and pores are identified. The inventive samples only have small pores in the reinforced zone and no defects in the interface layer.

Claims

1. A composite material (2) comprising:

at least one reinforcing zone (4) comprising core-rim tungsten titanium carbide (W,Ti)C, tungsten (WC) and a manganese steel matrix;
a manganese steel zone (6) that surrounds each of the reinforcing zones (4); and
an interface layer (8) positioned between each of the reinforcing zones (4) and the manganese steel zone (6);
characterized in that:
the average grain size of the (W,Ti)C particles in each of the reinforcing zones (4) is between 0.2-2μm and the average grain size of the WC particles in each of the reinforcing zones (4) is between 20-30 μm.

2. The composite material (2) according to claim 1 wherein the wt% of (W,Ti)C in each of the reinforcing zones (4) is between 80-98 and the wt% of WC in each of the reinforcing zones (4) is between 0-98.

3. The composite material (2) according to claim 1 or claim 2 wherein the composition of the manganese steel in manganese steel zone (6) has the chemical composition by weight of:

carbon: 0.5 to 2.0%;
manganese: 11 to 22%;
silicon: 0.2 to 1.0% ;
chromium: 1 to 2%;
Nickel: up to 0.6%
Molybdenum: up to 0.5%
and a balance of Fe.

4. The composite material (2) according to any of the previous claims wherein the hardness of the reinforcing zones (4) is between 900-1400 HV1 and the hardness of the manganese steel zone (6) is between 300 - 400 HV1 before work hardening.

5. The composite material (2) according to any of the previous claims wherein the thickness of each of the interface layer (6) is greater than 150 μm.

6. The composite material (2) according to any of the previous claims wherein the interface layer (8) is free of defects.

7. The composite material (2) according to any of the previous claims wherein wettability between the WC grains and the manganese steel and between the TiC grains and the manganese steel in the reinforcing zones (4) is >99%.

8. The composite material (2) according to any of the previous claims wherein each of the reinforcing zones has a volume of between 30-75 cm^3.

9. The composite material (2) according to any of the previous claims wherein at least 90% of the WC grains in the reinforcing zones (4) have different prismatic shapes.

10. The composite material (2) according to any of the previous claims wherein there are a plurality of reinforcing zones (4) and the distance between two neighbouring reinforcing zones is between 1-5 mm.

11. A wear part (14) comprising the composite material (2) according to any of claims 1-10.

12. A method of producing the composite material (2) according to any of claims 1-10 comprising the steps of:

a) mixing together 65-98 wt% tungsten, 3-90 wt% titanium, 3-20wt% carbon and 0-80 % catalysis powders
b) compacting the mixed powders together to form at least one compacts (20);
c) positioning and optionally fixing at least one compact (20) into the interior of a mold (22);
d) pouring molten casting manganese steel (24) into the mold (22) to surround the at least one compact (20) to initiate a self-propagating high temperature synthesis (SHS) reaction to produce a cast (26);
e) heat treating the cast (26)
f) quenching the cast (26)
characterized in that:
in step b) the powders are compacting with a pressure of between 400-700 mPa.

13. The method according to claim 12 wherein the catalysis is selected from Fe, Co, Ni, Mo, Cr, W, Al, or a mixture thereof.

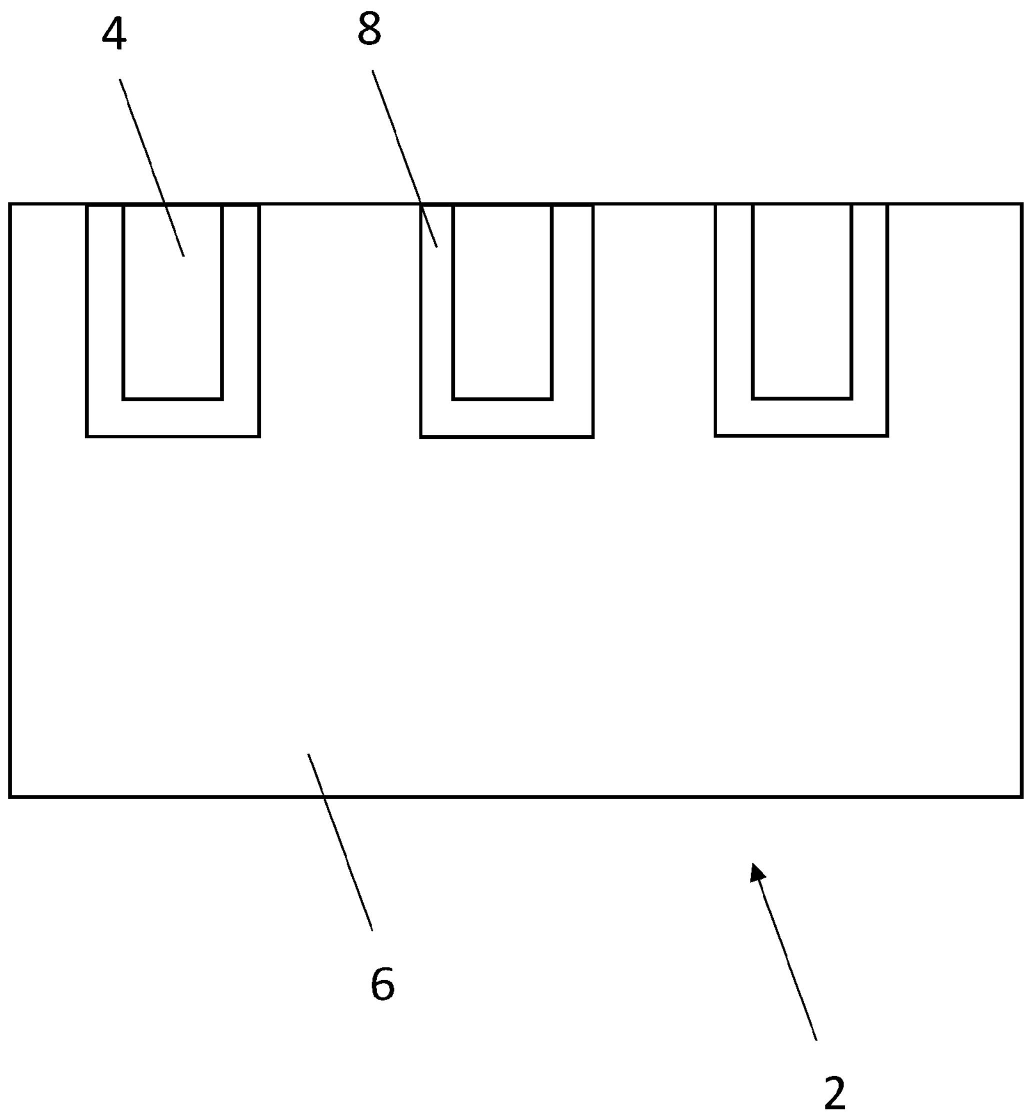

Fig. 1

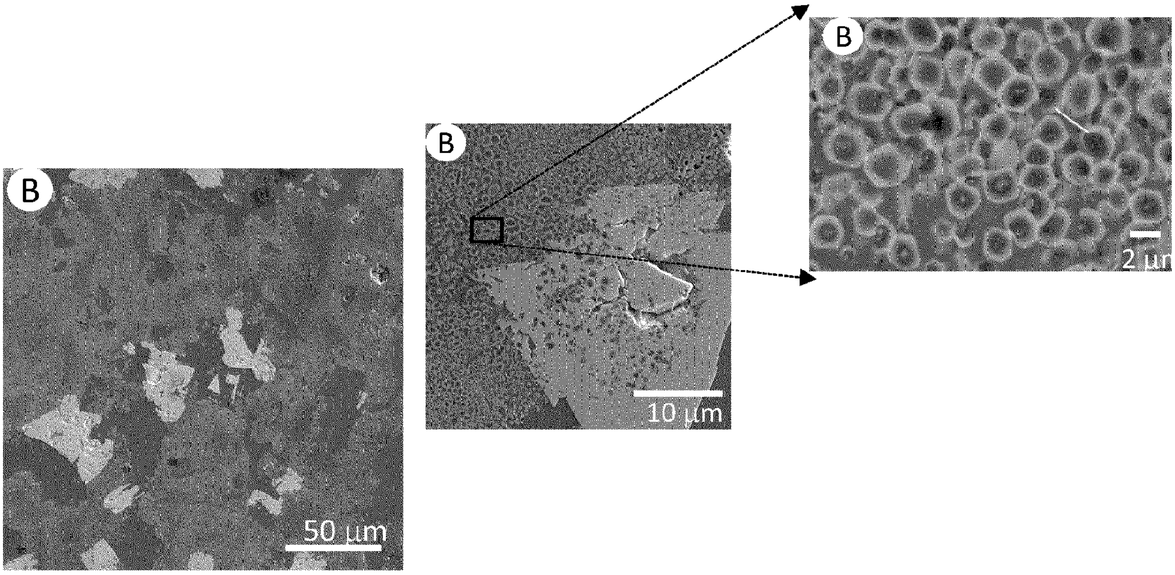

Fig. 2

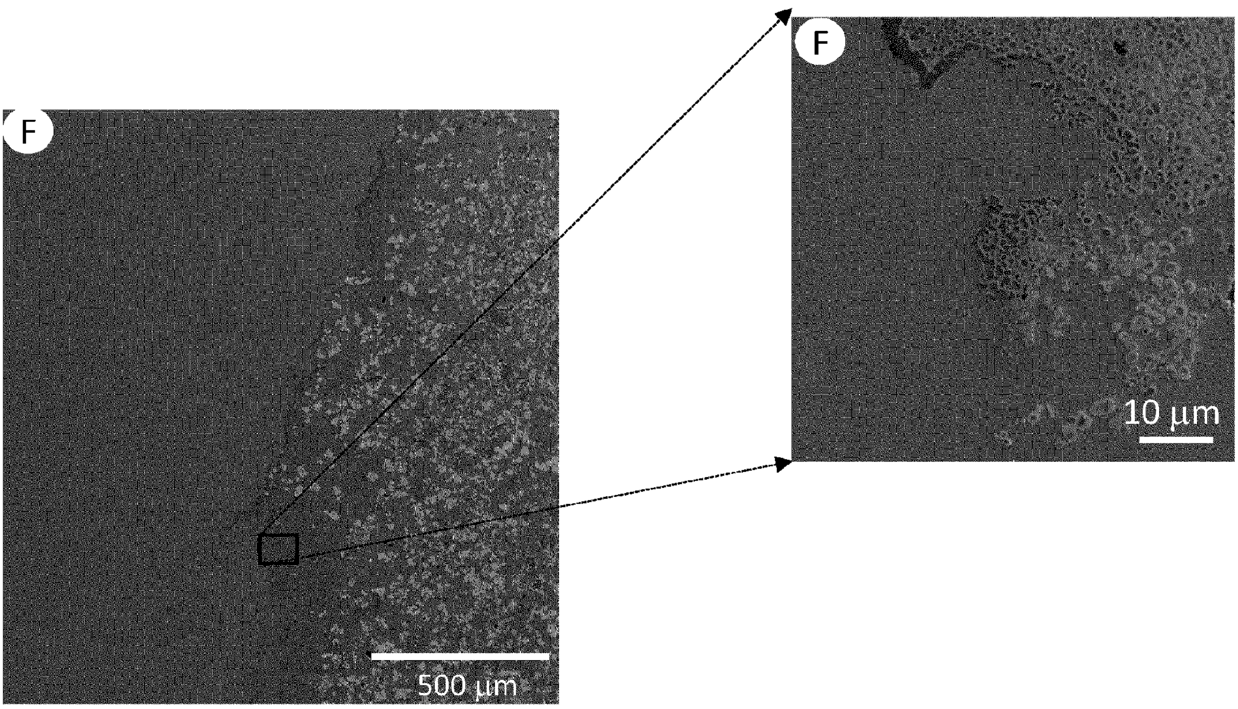

Fig. 3

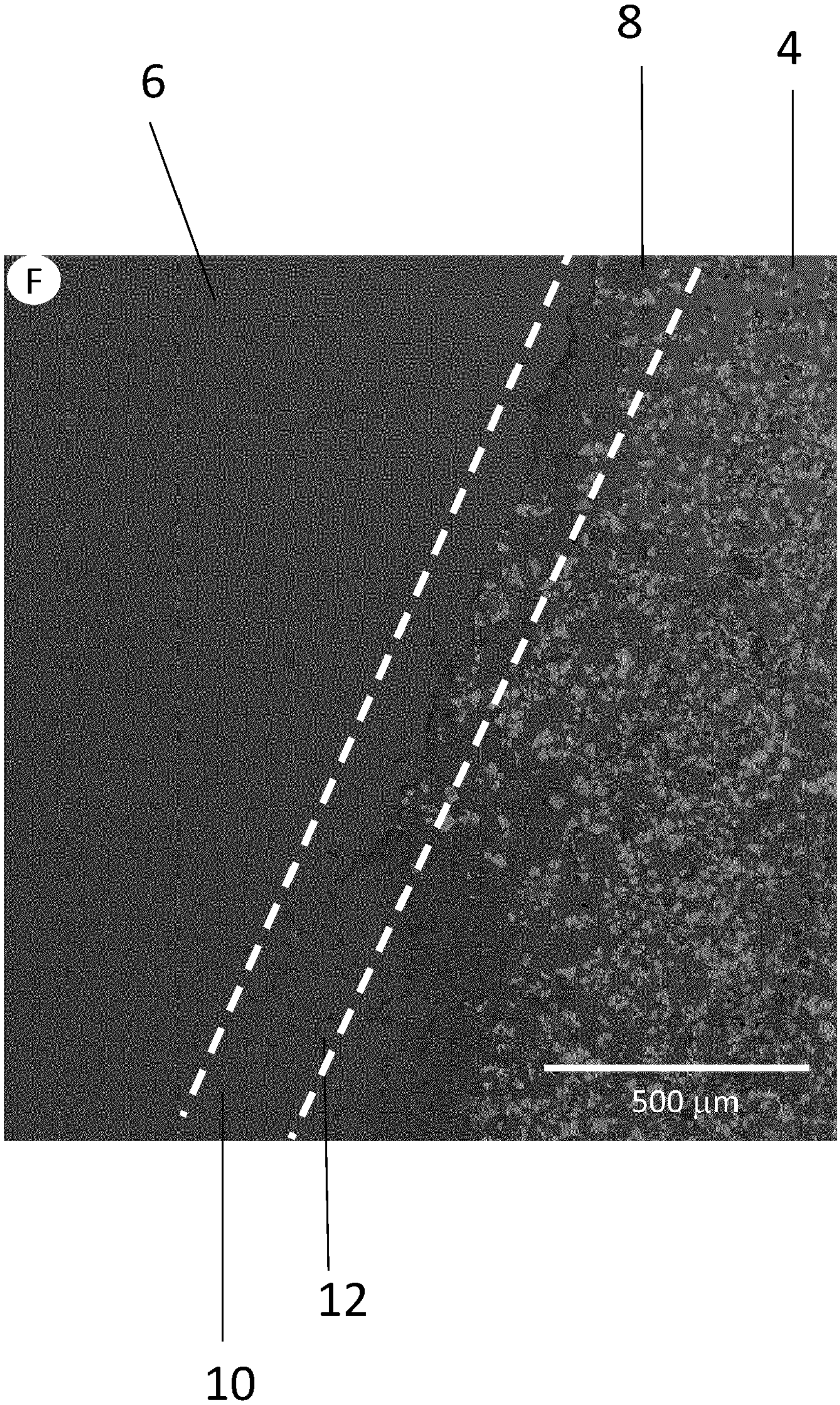

Fig. 4

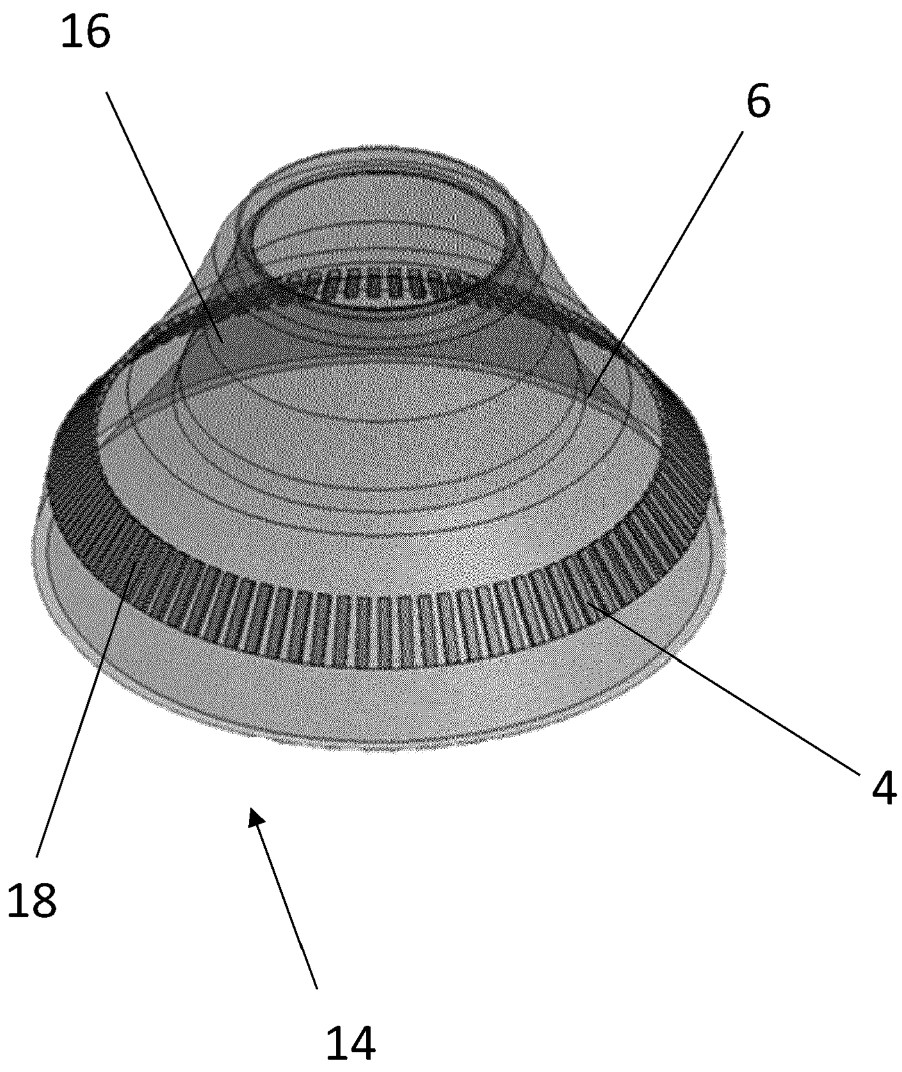

Fig. 5

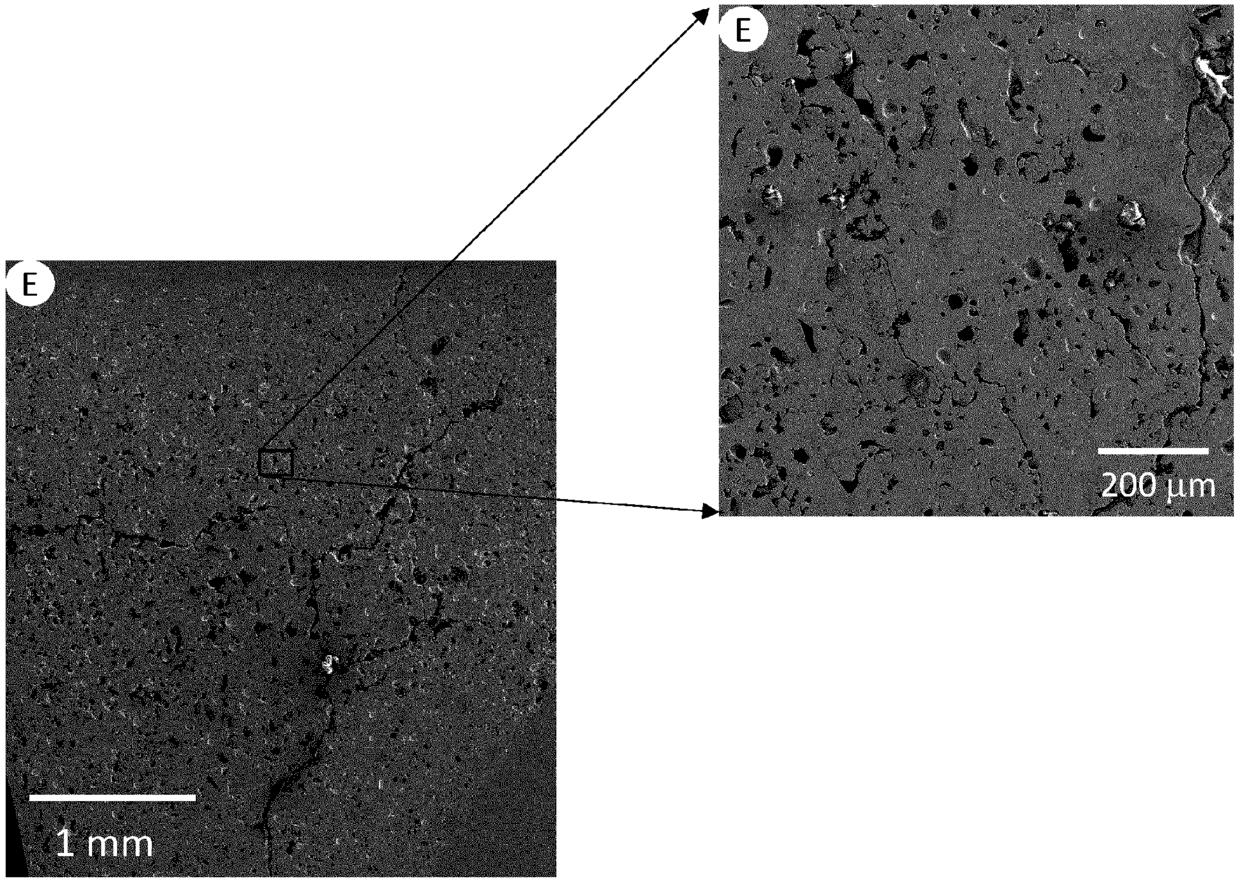

Fig. 6

Europäisches Patentamt
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EUROPEAN SEARCH REPORT

Application Number
EP 22 18 2569

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	US 2018/369905 A1 (OLEJNIK EWA [PL] ET AL) 27 December 2018 (2018-12-27) * paragraphs [0042], [0049]; claim 1; tables 6,7 * * Example 3 * -----	1-13	INV. B22D19/02 B22D19/14 B22F3/24 C21D6/00 C22C1/05 C22C29/00 C22C29/08 C22C29/10 C22C33/02 ADD. B22F5/00
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Place of search	Date of completion of the search	Examiner
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