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(54) BINDER REDISTRIBUTION WITHIN A CEMENTED CARBIDE MINING INSERT

(57) A method of redistributing the binder phase of a cemented carbide mining insert comprising one or more hard-phase components and a binder comprising the steps of: a) providing a green cemented carbide mining insert; b) applying at least one binder puller selected from a metal oxide or a metal carbonate to the surface of the green cemented carbide mining insert; and c) sintering the green cemented carbide mining insert characterized in that the metal oxide or metal carbonate is only applied to at least one local area on the surface of the green cemented carbide mining insert, also a cemented carbide having a hardness gradient and the use thereof.

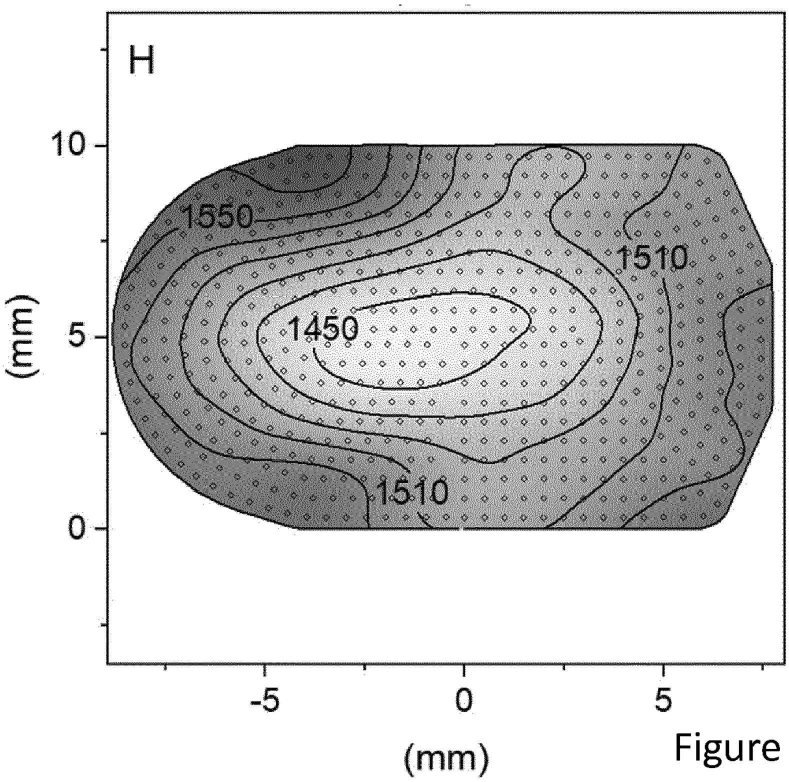

Figure 10

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Description

TECHNICAL FIELD

[0001] The present disclosure relates to a method of redistributing the binder within a cemented carbide mining insert, a cemented carbide mining insert with a hardness gradient and the use thereof.

BACKGROUND

[0002] Cemented carbide has a unique combination of high elastic modulus, high hardness, high compressive strength, high wear and abrasion resistance with a good level of toughness. Therefore, cemented carbide is commonly used in products such as mining tools. In general, the hardness and toughness of cemented carbide can be altered by changing the binder content and grain size of the hard phase. Typically, a higher binder content will increase the toughness of the cemented carbide but will decrease its hardness and wear resistance. A finer hard phase grain size will result in cemented carbide with a higher hardness which is more wear resistant, whereas a coarser hard phase grain size will not be as hard but will have higher impact resistance.

[0003] For maximised efficiency of cemented carbides mining inserts, a combination of these properties is desired and there are different demands on the material in different parts of the product. For example, in inserts for rock drilling and mineral cutting, it is desirable to have a tougher interior to minimize the risk of failure and a harder exterior to optimise wear resistance.

[0004] WO 2010/056191 discloses a method of forming a cemented carbide body comprising a hard phase and a binder phase, wherein at least one part of the intermediate surface zone has lower average binder content than a part further into the body.

[0005] There is however still a need for a method which is able to create even greater hardness gradients, able to tailor the gradient to a specific application and which could be applied even to non-symmetrical cemented carbide mining inserts. There is also a need to for a method which can redistribute the binder phase starting with a standard carbide powder which is stoichiometrically balanced with respect to carbon content.

SUMMARY

[0006] Thus, the present disclosure therefore provides a method of redistributing the binder phase within a cemented carbide mining insert comprising one or more hard-phase components and a binder comprising the steps of:

a) providing a green cemented carbide mining insert;

b) applying at least one binder puller selected from a metal oxide or a metal carbonate to the surface of the green cemented carbide mining insert; and

c) sintering the green cemented carbide mining insert;

characterized in that the metal oxide or metal carbonate is only applied to at least one local area on the surface of the green cemented carbide mining insert.

[0007] This method allows the binder to be re-distributed in a tailored and most favourable manner to provide optimal functionality to the cemented carbide mining insert. For examples, specific hardness profiles can be created for different application.

[0008] Additionally, the present disclosure relates a cemented carbide mining insert comprising one or more hard-phase components and a binder characterized in that there is a hardness gradient from a first part of the surface to a second part of the surface of the cemented carbide mining insert, wherein the first part of the surface is substantially opposing the second part of the surface, such that:

- the first part of the surface is between 30HV3 softer and 80HV3 harder than the second part of the surface; and
- the first part of the surface is between 5 and 120 HV3 harder than the bulk; and
- the second part of the surface is between 20HV3 and 70HV3 harder than the bulk.

FIGURES

[0009]

Figure 1: Schematic drawing of an insert showing the binder puller and binder pusher applied symmetrically to opposing sides.

Figure 2: Schematic drawing of an insert showing the binder puller and binder pusher applied asymmetrically to opposing sides.

Figure 3: HV3 iso-hardness plots for sample A disclosed in example 1.

Figure 4: HV3 iso-hardness plots for sample B disclosed in example 1.

Figure 5: HV3 iso-hardness plots for sample C disclosed in example 1.

Figure 6: HV3 iso-hardness plots for sample D disclosed in example 1.

Figure 7: HV3 iso-hardness plots for sample E disclosed in example 1.

Figure 8: HV3 iso-hardness plots for sample F disclosed in example 1.

Figure 9: HV3 iso-hardness plots for sample G disclosed in example 1.

Figure 10: HV3 iso-hardness plots for sample H disclosed in example 1.

Figure 11: HV3 iso-hardness plots for sample I disclosed in example 1.

Figure 12: HV3 iso-hardness plots for sample J disclosed in example 1.

Figure 13: HV3 iso-hardness plots for sample K disclosed in example 1.

Figure 14: Schematic drawing of an insert showing where the binder puller was applied in example 1.

Figure 15: HV3 centre line hardness profiles for samples A, B and C disclosed in example 1.

Figure 16: HV3 centre line hardness profiles for samples D, E and F disclosed in example 1.

Figure 17: HV3 centre line hardness profiles for samples G, H and I disclosed in example 1.

Figure 18: HV3 centre line hardness profiles for samples J and K disclosed in example 1.

Figure 19: HV5 iso-hardness plots for example 2 wherein the binder puller and binder pusher are applied asymmetrically.

Figure 20: Schematic drawing of the set up for the pendulum hammer test.

Figure 21: Cobalt concentration profiles as discussed in example 5 for samples D and G.

Figure 22: Chromium concentration profiles as discussed in example 5 for samples D and G.

Figure 23: Cr/Co concentration profiles as discussed in example 5 for samples D and G.

Figure 24: Cobalt concentration profiles as discussed in example 5 for sample K.

Figure 25: Chromium concentration profiles as discussed in example 5 for sample K.

DETAILED DESCRIPTION

[0010] According to one aspect, the present disclosure relates to a method of redistributing the binder phase of a cemented carbide mining insert comprising a WC hard-phase, optionally one or more further hard-phase components and a binder comprising the steps of:

a) providing a green cemented carbide mining insert;

b) applying at least one binder puller selected from a metal oxide or a metal carbonate to the surface of the green cemented carbide mining insert; and

c) sintering the green cemented carbide mining insert;

characterized in that the metal oxide or metal carbonate is only applied to at least one local area on the surface of the green cemented carbide mining insert.

[0011] The one or more further hard-phase components may be selected from TaC, TiC, TiN, TiCN, NbC, CrC. The binder phase may be selected from Co, Ni, Fe or a mixture thereof, preferably Co and / or Ni, most preferable Co. The carbide mining insert has a suitable binder content of from about 4 to about 30 wt%, preferably from about 5 to about 15 wt%. The carbide mining insert may optionally also comprise a grain refiner compound in an amount of ≤20 wt% of the binder content. The grain refiner compound is suitably selected from the group of carbides, mixed carbides, carbonitrides or nitrides of vanadium, chromium, tantalum and niobium. With the remainder of the carbide mining insert being made up of the one or more hard-phase components.

[0012] In one embodiment of the method, the cemented carbide mining insert contains a hard phase comprising at least 80 wt% WC, preferably at least 90 wt%.

[0013] In the present disclosure, the term "green" refers to a cemented carbide mining insert produced by milling the hard phase component(s) and the binder together and then pressing the milled powder to form a compact cemented carbide mining insert, which has not yet been sintered. The term "binder puller" refers to a substance which when applied to the surface of the cemented carbide mining insert will cause the binder to migrate towards that surface during the sintering step, i.e. the binder is pulled in the direction towards the surface where the "binder puller" has been applied. The binder puller works by locally consuming carbon which causes the binder to flow from the areas having normal carbon levels to the local area where the carbon level has been depleted.

[0014] The inventors have found that applying the binder puller, which is selected from a metal oxide or a metal carbonate, to the surface of the green cemented carbide mining insert in at least one local area, that carbon is locally consumed in this area during sintering which causes the formation of a carbon potential. This will promote the migration of the binder phase from areas having normal or higher levels of carbon to the local area which has a depleted carbon level. This will therefore form a binder rich region on a local area of the surface of the cemented carbide mining insert. The surface of the green cemented carbide mining insert where the binder puller is applied is referred to as the "oxide / carbonate doped" surface. It is well known that binder rich regions and binder depleted regions will be in tensile stress and compressive stress respectively after sintering. It would normally not be favourable to introduce tensile stresses. However, the inventors have found that after a treatment, such as centrifugal tumbling, high levels of compressive stress, down to at least 1mm depth below tumbled surface, can be introduced to counteract the tensile stresses present. Therefore, the benefit of applying the binder puller can be gained without the detrimental effect of introducing tensile stresses.

[0015] The "at least one local area on the surface of the green cemented carbide mining insert" could be at any position on the surface, for example the tip, the base or the side depending on where the requirement to create an increase in binder content is. The binder puller may be applied to one or more local areas on the surface of the cemented carbide mining insert depending on whether the desired effect is to create a local increase in toughness or wear resistance. Each "local area" may be 0.5-85% of the total surface area of the cemented carbide mining insert, preferably 3-75%.

[0016] The sintering temperature is suitably from about 1000°C to about 1700°C, preferably from about 1200°C to about 1600°C, most preferably from about 1300°C to about 1550°C. The sintering time is suitably from about 15 minutes to about 5 hours, preferably from about 30 minutes to about 2 hours.

[0017] In one embodiment of the method, the binder puller, being a metal oxide or metal carbonate is selected from Cr_2O_3, MnO, MnO_2, MoO_2, Fe-oxides, NiO, NbO_2, V_2O_3, $MnCO_3$, $FeCO_3$, $CoCO_3$, $NiCO_3$, $CuCO_3$ or Ag_2CO_3. It would also be possible to alternatively apply a metal to the surface of the green cemented carbide mining insert which upon heating, during the sintering step, would form an oxide. The selection of the metal oxide or metal carbonate will influence the properties of the cemented carbide post sintering e.g. deformation hardening, heat resistance and / or corrosion resistance and the selection can be made to be best suited to the required application. Metal carbonates would be selected if the equivalent metal oxide is toxic and the metal carbonate is not. In this method, there is a high degree of freedom as to where the binder puller is applied, for example it could be applied in or away from the wear zones of the carbide tool, depending on whether the metal in the oxide or carbonate improves the wear resistance of the cemented carbide or not.

[0018] In one embodiment of the method, the binder puller is Cr_2O_3. Using Cr_2O_3 as the binder puller has the advantage that a chromium alloy rich surface layer will form, which has an enhanced response to a tumbling treatment. Therefore, higher compressive stresses will be introduced, and the wear properties of the cemented carbide mining insert will be improved. The Cr_3O_2 contributes towards grain refinement and hence, a reduced grain size is measured on the side of the insert where the Cr_3O_2 has been applied.

[0019] The metal oxide or metal carbonate is suitably provided onto the surface or surfaces in an amount of from about 0.1 to about 100 mg/cm^2, preferably in an amount of from about 1 to about 50 mg/cm^2. The starting cemented carbide powder blend should suitably have a carbon balance equivalent to 0.95<Com/%Co<1 or have an excess of carbon that would compensate for the carbon reduction from the application of the oxide or carbonate. Com is 100*S, $_{Insert}/\sigma_{S,\ Cobalt}$ wherein σ_S is the weight specific saturation magnetization measured in Tm^3/kg and $\sigma_{S,\ Cobalt}$ = 2.01E-4 Tm^3/kg. Com is measured in a Foerster Koerzimat CS.1097 unit.

[0020] In one embodiment of the method, the binder puller is applied to the top of the cemented carbide mining insert. In another embodiment of the method, the binder puller is applied to the side of the cemented carbide mining insert. Therefore, the properties of the cemented carbide mining insert can be tailored to be suited to the application. The binder puller is likely chosen to be applied to the position on the surface of the cemented carbide mining insert that is exposed to the highest wear.

[0021] In one embodiment, the method further comprises the step between steps a) and b) of applying at least one binder pusher to at least one different local area on the surface of the green cemented carbide mining insert. In the present disclosure, the term "binder pusher" refers to a substance, which when is applied to the surface of the carbide mining insert, will cause the binder to migrate away from that surface during the sintering step, i.e. the binder is pushed in the direction away from the surface where the "binder pusher" has been applied. The combined application of a binder puller applied to at least one local area on the surface and a binder pusher to the at least one different local area on the surface of the cemented carbide mining insert would mean that the green cemented carbide mining insert could be made having a carbon content within the standardly used ranges, such as 0.95<Com/%Co<1, and using standard processes therefore allowing for efficiency in the production. Preferably the migration takes places through the depth of the insert, rather than along the surface of the insert.

[0022] In one embodiment of the method the binder pusher is selected from a metal carbide, a carbon powder, such as graphite, or a mixture thereof. The application of the metal carbide, the carbon powder or the mixture thereof will create a carbon gradient, which will result in the cobalt migrating away from the surface to which it was applied, i.e. the binder is pushed away from that surface of the carbide towards the inner bulk in this local area(s). Selection of a metal carbide will have the additional effect of grain refinement in the applied local area whereas the selection of a carbon powder will have the effect of promoting grain growth in the applied local area(s). The resulting difference in the grain growth gradient created is not as significant as the effect that the binder gradient has on the hardness gradient.

[0023] In one embodiment, the binder pusher is a combination of a metal carbide and a carbon powder. The weight ratio of the metal carbide to the carbon powder is suitable from about 0.05 to about 50, preferably from about 0.1 to about 25, more preferably from about 0.2 to about 15 and even more preferably from about 0.3 to about 12 and most preferably from about 0.5 to 8. The metal carbide is suitably provided onto the surface or surfaces in an amount of from about 0.1 to about 100 mg/cm^2, preferably in an amount of from about 1 to about 50 mg/cm^2. The carbon powder is suitably provided onto the surface or surfaces in an amount of from about 0.1 to about 100 mg/cm^2, preferably in an amount of from about 0.5 to about 50 mg/cm^2.

[0024] If only a carbon powder, such as graphite, is selected as the binder pusher this would lead to a coarsening of the hard phase grains in the area where it has been applied. This would result in being able to achieve a combination of high wear resistance and improved thermal conductivity in the zones on the mining button exposed to the rock being worked and high toughness behind these zones.

[0025] In one embodiment of the method the metal carbide is selected from a carbide of chromium, vanadium, magnesium, iron or nickel, preferably a carbide of chromium, such as Cr_3C_2, $Cr_{23}C_6$, Cr_7C_3.

[0026] Selection of a metal carbide, such as Cr_3C_2, in combination with a carbon powder is advantageous as this combination will cause the binder to migrate from the doped surface and the addition of the carbon prevents the grain refining effect of the Cr_3C_2.

[0027] During sintering any metal carbide applied to the surface of the green cemented carbide mining insert should substantially dissolve.

[0028] In one embodiment of the method, the binder puller and the binder pusher are applied to different local areas of the surface of the cemented carbide mining insert. By applying the binder puller and binder pusher to different local areas a binder gradient between the two surfaces is created. This gradient in binder will mean that a hardness gradient is created, with a harder, binder depleted surface formed where the binder pusher has been applied and a tougher, binder rich surface formed where the binder puller has been applied. The combined application of a binder puller and binder pusher to different local areas of the surface of the cemented carbide mining insert is particularly useful in creating a hardness gradient in larger carbide bodies where previously known methods would not create a sufficiently deep gradient. The binder puller may be applied to a selected area on the surface of the green cemented carbide mining insert and the binder pusher may be applied to a different selected area on the surface of the green cemented carbide mining insert. The binder pusher could be placed in the wear zone to reduce the binder content and therefore improve wear resistance in that area or where it is favourable to have higher thermal conductivity. The local application of the binder puller and the binder pusher presents unique possibilities to create carbide bodies with tailor made properties.

[0029] Another benefit of using this method is that self-sharpening zones can be created if the wear rates on different areas of the surface are uneven. The contact pressure between a worn insert and the rock increases with a sharper tip as there is a reduced area of contact. With a homogenous material, the wear causes the formation of a wear flat that often needs re-sharping using diamond grinding tools. Re-sharpening by grinding is costly and requires that the drill bits are unmounted. By having non-homogeneous material properties, it is possible to have zones that wear faster and zones that wear slower. If the material properties of the mining inserts are tailored to having a wear surface that has areas with different wear rates, the formation of wear flats are avoided, and consequently sharper wear surfaces are created in comparison to using homogeneous materials.

[0030] In one embodiment of the method, the binder puller and the binder pusher are applied to substantially opposing local areas of the surface of the cemented carbide mining insert.

[0031] In one embodiment, the method of applying the binder puller and the binder pusher is selected from pressing, dipping, painting, spraying (air brushing), stamping or 3D printing. Dipping could be done with or without masking. The binder puller and binder pusher may be applied to the surface of green cemented carbide mining insert in the form of liquid dispersions or a slurry. In such as case, the liquid phase is suitably water, an alcohol or a polymer such as polyethylene glycol. The concentration of the slurry is suitably 5-50 wt% of the powder in the liquid phase, such as 15-40 wt%. This range is advantageous so that a sufficient effect of the binder puller or pusher is realised. If the powder content is too high, then there may be issues with clogging and lumping within the liquid dispersion or slurry. Alternatively, they could be introduced as a solid substance, for example by adding the powder into the pressing mould in a suitable position. The powder could be mixed with a hard-phase powder, for example a WC-based powder. The binder puller and the binder pusher could also be applied to the cemented carbide mining insert in any other suitable way. The compositions and concentration of the slurry and the way it is applied influences the control of the redistribution of the binder and therefore allows the hardness profile of the cemented carbide mining insert to be controlled.

[0032] In one embodiment of the method, the binder puller is applied to a first part of the surface (10) and the binder pusher is applied to a second part of the surface (20) rotationally symmetrically as shown in Figure 1.

[0033] In one embodiment of the method, the binder puller is applied to a first part of the surface (10) and the binder pusher is applied to a second part of the surface (20) rotationally asymmetrically as shown in Figure 2.

[0034] As there is flexibility in where the binder puller and binder pusher are applied, this allows tailoring of the position of the "wear zone", i.e. the position on the surface having the most enhanced wear properties. For example, the wear zone could be on either the top or the side of the insert depending where the interaction between the cemented carbide mining insert and rock being drilled is the highest. This will vary depending on the application it is being used for and the position of the cemented carbide mining insert on the rock drill bit.

[0035] Cemented carbide mining inserts are subjected to high compressive loading. Consequently, surface cracking caused by small cracks growing to a critical size through repeated intermittent high loading is a common cause of insert failure. It is known that introducing compressive stress into the surface of the insert can reduce this problem as the presence of the compressive stress can prevent crack growth and wear of the material. Known methods of introducing compressive stress into surfaces of a cemented carbide mining insert include shot peening, vibration tumbling and centrifugal tumbling. These methods are all based on mechanical impact or deformation of the outer surface of the body and will increase the lifetime of the cemented carbide mining inserts.

[0036] In one embodiment of the method, post sintering the cemented carbide mining insert is treated with a tumbling process. The cemented carbide mining inserts are subjected to a posttreatment surface hardening which introduces high levels of compressive stress into the inserts. For mining inserts, this would normally be a tumbling treatment, which could be centrifugal or vibrational. However, other post-treatments surface hardening methods, e.g. shot peening, could be used. Following tumbling, normally an increase in magnetic coercivity (kA/m) is measured.

[0037] A "standard" tumbling process would typically be done using a vibrational tumbler, such as a Reni Cirillo RC 650, where about 30 kg inserts would be tumbled at 50 Hz for about 40 minutes. An alternative typical "standard" tumbling process would be using a centrifugal tumbler such as the ERBA-120 having a closed lid at the top and has a rotating disc at the bottom. Cooling water with antioxidants is continuously fed with 5 liters per minute when the disc (Ø600mm) rotates. Tungsten carbide media can also be added to increase the load in the tumbler. The rotation causes the inserts to collide with other inserts or with any media added. The collision and sliding removes sharp edges and causes strain hardening. For "standard" tumbling using a centrifugal tumbler the tumbling operation would typically be run from 120 RPM for at least 20 minutes.

[0038] In one embodiment of the method, the tumbling process is a "High Energy Tumbling" (HET) method. To introduce higher levels of compressive stresses into the cemented carbide mining insert a high energy tumbling process may be used. There are many different possible process set ups that could be used to introduce HET, including the type of tumbler, the volume of media added (if any), the treatment time and the process set up, e.g. RPM for a centrifugal tumbler etc. Therefore, the most appropriate way to define HET is in terms of "any process set up that introduces a specific degree of deformation hardening in a homogenous cemented carbide mining insert". In the present disclosure, HET is defined as a tumbling treatment that would introduce a hardness change, measured using HV3, after tumbling ($\Delta HV3\%$) of at least:

$$\Delta HV3\% = 9.72 - 0.00543 * HV3_{bulk} \quad \text{(equation 1)}$$

Wherein:

$$\Delta HV3\% = 100 * (HV3_{0.3mm} - HV3_{bulk}) / HV3_{bulk} \quad \text{(equation 2)}$$

[0039] $HV3_{bulk}$ is an average of at least 30 indentations points measured in the innermost (centre) of the cemented carbide mining insert and $HV3_{0.3mm}$ is an average of at least 30 indentation points at 0.3mm below the tumbled surface of the cemented carbide mining insert. This is based on the measurements being made on a cemented carbide mining insert having homogenous properties. By "homogeneous properties" we mean that post sintering the hardness different is no more than 1% from the surface zone to the bulk zone. The tumbling parameters used to achieve the deformation hardening described in equations (1) and (2) on a homogenous cemented carbide mining insert would be applied to cemented carbide bodies having a gradient property.

[0040] HET tumbling may typically be performed using an ERBA 120, having a disc size of about 600 mm, run at about 150 RPM if the tumbling operation is either performed without media or with media that is larger in size than the inserts being tumbled, or at about 200 RPM if the media used is smaller in size than the inserts being tumbled; Using a Rösler tumbler, having a disc size of about 350 mm, at about 200 RPM if the tumbling operation is either performed without media or with media that is larger in size than the inserts being tumbled, or at about 280 RPM if the media used is smaller in size than the inserts being tumbled. Typically, the parts are tumbled for at least 40-60 minutes. HET enables use of binder enriched surface zones as the compressive stresses introduced from the HET counteract the tensile stresses formed by the higher thermal expansion coefficient in the binder enriched zones adjacent to binder depleted zones.

[0041] Another aspect of the present invention relates to a cemented carbide mining insert comprising one or more hard-phase components and a binder wherein there is a hardness gradient from a first part of the surface to a second part of the surface of the cemented carbide mining insert, wherein the first part of the surface is substantially opposing the second part of the surface, such that post sintering:

- the first part of the surface is between 30HV3 softer and 80HV3 harder than the second part of the surface; and
- the first part of the surface is between 5 and 120 HV3 harder than the bulk; and
- the second part of the surface is between 20HV3 and 70HV3 harder than the bulk.

[0042] The hardness measurements are post sintering and prior to any post sintering treatment, such as tumbling.

[0043] In one embodiment, the hardness gradient is such that:

- the first part of the surface is between 2% softer and +6% harder than the second part of the surface; and
- the first part of the surface is between +0.5 and +10% harder than the bulk; and
- the second part of the surface is between +0.3% and 6% harder than the bulk.

[0044] The first part of the surface is the surface where the binder puller has been applied to form an oxide / carbonate doped surface. The second part of the surface is the surface opposing where the binder puller has been applied (the side opposing the oxide / carbonate doped surface). Optionally, the second part of the surface could be a surface where a binder pusher has been applied to form a carbide doped surface.

[0045] This is also shown in table 1 below:

Table 1: Hardness differences

	Hardness difference HV3	**Hardness difference (%)**
First part of the surface (oxide / carbonate doped surface) vs second part of the surface (side opposing oxide / carbonate doped surface)	First part of the surface (the oxide / carbonate doped surface) is between 30HV3 softer and 80HV3 harder.	First part of the surface (the oxide / carbonate doped surface) is between 2% softer and 6% harder.

(continued)

	Hardness difference HV3	**Hardness difference (%)**
First part of the surface (oxide / carbonate doped surface) vs bulk	First part of the surface (the oxide / carbonate doped surface) is between 5HV3 and 120HV3 harder than the bulk.	First part of the surface (the oxide / carbonate doped surface) is between 0.5% and 10% harder than the bulk.
Second part of the surface (side opposing oxide / carbonate doped surface) vs bulk	Second part of the surface (the side opposing the oxide / carbonate doped surface) is between 20HV3 and 70HV3 harder than the bulk.	Second part of the surface (the side opposing the oxide / carbonate doped surface) is between 0.3% and 6% harder than the bulk.

[0046] By the term "bulk" is herein meant the cemented carbide of the innermost part (centre) of the rock drill insert and for this disclosure is the zone having the lowest hardness.

[0047] The hardness of the cemented carbide inserts is measured using Vickers hardness mapping. The cemented carbide bodies, are sectioned along the longitudinal axis and polished using standard procedures. Vickers indentations at a 3 kg load are then symmetrically distributed over the polished section. The rhombuses in figures 3-13 and 16 show the locations of the HV3 indentations. The hardness measurements are performed using a programmable hardness tester, KB30S by KB Prüftechnik GmbH calibrated against HV3 test blocks issued by Euro Products Calibration Laboratory, UK. Hardness is measured according to ISO EN6507.
HV3 measurements were done in the following way:

- Scanning the edge of the sample.
- Programming the hardness tester to make indentations at specified distances from the edge of the sample.
- Indentation with 3 kg load at all programmed co-ordinates.
- The computer moves the stage to each co-ordinate with an indentation and runs auto adjust light, auto focus and the automatically measures the size of each indentation.
- The user inspects all the photos of the indentations for focus and other matters that disturb the result.

[0048] The HV3 measurements for the oxide / carbonate doped surface and side opposing the oxide / carbonate doped surface were measured at a distance between 0.3 and 0.8 mm below the surface, with 10-40 indentations being made and then the average HV3 measurement calculated. The HV3 measurement for the bulk is measured in near the centre of the polished section at the position having the lowest hardness, over an area of about 1.5-2 mm^2, taking the average from about 15-20 indentations.

[0049] In one embodiment, the maximum concentration (%binder-max) is less than 20% higher than the minimum concentration (%binder-min) within the cemented carbide mining insert.

[0050] In one embodiment, the %binder-min (e.g. minimum Co concentration / %Co-min) is at a depth, in percentage of the total height of the sintered cemented carbide mining insert, of between 1-50% from the first part of the surface, preferably between 5-40%. The %binder-min is typically at a depth of 0.5-10 mm, preferably 0.8-7 mm from the first part of the surface.

[0051] In one embodiment, there are two peaks in binder concentration, one near the surface and one in the bulk of the cemented carbide mining insert. There is a first maximum binder concentration (%binder-max1) (e.g. %Co-maxl) at the first part of the surface (e.g. at the oxide / carbonate doped surface) and a second maximum binder concentration (%binder-max2) (e.g. %Co-max2) at a depth, in percentage of the total height of the cemented carbide mining insert, of between 15-75% from the first part of the surface (e.g. from the oxide / carbonate doped surface), preferably between 20-65%. In one embodiment, %binder-max1 ≥ %binder-max2. In an alternative embodiment, %binder-max1 ≤ %binder-max2. The %binder-max2 is typically 2-15 mm from the first part of the surface, preferably between 4 -12 mm. The difference in the height of the %binder-min and %binder-max2 is typically between 1.5-12 mm, preferably between 2.5-10 mm.

[0052] In one embodiment, there is a first chromium concentration maximum (%Cr-max1) at the first part of the surface (e.g. at the oxide/carbonate doped surface). In one embodiment, there is additionally a second chromium concentration maximum (%Cr-max2) at the surface second part of the surface (e.g. the surface opposing to oxide/carbonate doped surface), wherein %Cr-max1>%Cr-max2. The chromium concentration minimum (%Cr-min) is located between %Cr-max1 and %Cr-max2, in the bulk of the cemented carbide mining insert. The %Cr-min is preferably at a depth, in percentage of total height of the sintered cemented carbide mining insert, of 40-99%, more preferably at a depth of

50-98% from the first part of the surface. "At the surface" is defined as up to 0.3 mm from the surface.

[0053] The chemical concentrations within the cemented carbide mining insert are measured using wavelength dispersive spectroscopy (WDS) along the centreline of a cross sectioned cemented carbide mining insert.

[0054] Another aspect of the present disclosure relates to the use of the cemented carbide mining insert as described hereinbefore or hereinafter for rock drilling or oil and gas drilling.

[0055] The following examples are illustrative, non-limiting examples.

EXAMPLES

Example 1 - only binder puller applied

[0056] Table 2 shows a summary of the samples analysed:

Table 2: Summary of samples measured

Sample	Powder blend	Slurry applied to surface	Tumbling treatment
A	94 wt% WC + 6 wt% Co	None	None
B	94 wt% WC + 6 wt% Co	None	Standard
C	94 wt% WC + 6 wt% Co	None	HET
D	94 wt% WC + 6 wt% Co	Carbide doped slurry	None
E	94 wt% WC + 6 wt% Co	Carbide doped slurry	Standard
F	94 wt% WC + 6 wt% Co	Carbide doped slurry	HET
G (invention)	94 wt% WC + 6 wt% Co	Oxide doped slurry	None
H (invention)	94 wt% WC + 6 wt% Co	Oxide doped slurry	Standard
I (invention)	94 wt% WC + 6 wt% Co	Oxide doped slurry	HET
J (invention)	89 wt% WC + 11 wt% Co	Oxide doped slurry	None
K (invention)	89 wt% WC + 11 wt% Co	Oxide doped slurry	HET

[0057] For sample A to I in Table 2 the cemented carbide inserts were produced using a powder blend having a composition of 94 wt% WC and 6 wt% Co. The WC powder grain size measured as FSSS was before milling between 5 and 7 μm. The WC and Co powders were milled in a ball mill in wet conditions, using ethanol, with an addition of 2 wt% polyethylene glycol (PEG 8000) as organic binder (pressing agent) and cemented carbide milling bodies. After milling, the slurry was spray-dried in N_2-atmosphere and then uniaxially pressed into mining inserts having a size of about 12 mm in outer diameter (OD) and about 17-20 mm in height (sample B = 18.7mm height; sample C = 17.4mm height; sample D = 18.7mm height; sample E and F =17.4mm height; samples G, H and I = 20.2mm height) with a weight of approximately 14-17g each with a spherical dome ("cutting edge") on the top. The inserts were ground on the negative part but leaving the dome and bottom part in an as-sintered condition.

[0058] Samples A, B and C had no slurry applied. Samples D, E and F are examples are comparative examples where only a binder pusher, in the form of a "carbon doped slurry", was applied, using a dipping technique, to the top, domed surface of the cemented carbide mining inserts. The carbon doped slurry consisted of 25 wt% Cr_3C_2 and 5 wt% graphite dispersed in water and was applied to the cemented carbide insert so that about 60% of the total insert length was exposed to the carbide doped slurry. Samples F, G and H are examples of the invention where only a binder puller is applied, the samples were treated by applying an "oxide doped slurry", comprising 30 wt% Cr_3O_2 and 70 wt% PEG300, to the domed surface of the cemented carbide insert in an amount of between 0.25 -0.28 mg/mm^{2,} with about 60% of the total insert length exposed to the oxide slurry. All the samples were sintered using Sinter-HIP in 55 bar Ar-pressure at 1410°C for 1 hour. For these examples, the slurry was applied symmetrically, i.e. applied to the domed surface extending an equal distance down the each of the sides of the insert.

[0059] Samples B, E and H were tumbled using "standard tumbling", using an ERBA-120 centrifugal tumbler at 120 RPM for 30 minutes. Samples C, F and I were tumbled using "High energy tumbling (HET)", using an ERBA-120 centrifugal tumbler 170 RPM or 40 minutes.

[0060] Samples J and K are examples of the invention where the cemented carbide inserts have a higher binder content. The cemented carbide inserts were produced using a powder blend having a composition of 89 wt% WC and 11 wt% Co. The WC powder grain size measured as FSSS was before milling between 8 and 12 μm. The WC and Co powders were milled in a ball mill in wet conditions, using ethanol, with an addition of 2 wt% polyethylene glycol (PEG 8000) as organic binder (pressing agent) and cemented carbide milling bodies. After milling, the slurry was spray-dried in N_2-atmosphere and then uniaxially pressed into mining inserts having a size of about 17 mm in outer diameter (OD) and about 22 mm in height, with a weight of approximately 31 g each with a conical tip ("cutting edge") on the top. The inserts were ground on the cylindrical part but leaving the conical tip and the bottom part in an as-sintered condition.

[0061] Samples J and K are examples of the invention where only a binder puller is applied, the samples were treated by applying an "oxide doped slurry", using a dipping technique, comprising 30 wt% Cr_3O_2 and 70 wt% PEG300, covering the conical tip and part of the cylindrical section in an amount of between 0.25-0.35 mg/mm^2 so that approximately 75% of the total length of the insert was exposed to the oxide doped slurry. The samples were sintered using Sinter-HIP in 55 bar AR-pressure at 1410°C for 1 hour. For these examples, the slurry was applied symmetrically, i.e. applied to the domed surface extending an equal distance down the each of the sides of the insert.

[0062] Samples K was tumbled using "High energy tumbling (HET)", in a Rösler model FKS 04.1 E-SA centrifugal tumbler at 250 RPM for 60 minutes with 50kg of media in the form of carbide balls of 7mm in diameter.

[0063] Figures 3-13 show the HV3 iso-hardness maps for samples A - I respectively and Figures 15-18 shows the centre lines plots for samples A-K from Table 2. The hardness profiles of the cemented carbide inserts are as described Table 1. The binder puller was applied to the tip (30) of the cemented carbide mining insert, as shown in figure 14.

[0064] It can be seen that the hardness profiles of the present invention are very different to the prior art and show that there is a softer core zone in the bulk and higher hardness at both the top and the bottom of the cemented carbide mining insert.

Example 2 - binder puller and binder pusher applied

[0065] Cemented carbide inserts were formed using the same starting material as samples J and K (89 wt% WC + 11 wt% Co) and method as described in table 2 / example 1. Mining inserts were formed by uni-axial pressing having a length of 24 mm and a cylindrical base of 19 mm diameter and a spherical (half dome) tip. Two PEG slurries were made up, the first a "binder puller", which consisted of 30%Cr_2O_3+PEG and the second a "binder pusher", which consisted of 25%Cr_3C_2+5%C+PEG. The slurries were then applied to the surface of the inserts by dipping the inserts into the slurry. The inserts were then sintered at 1410°C, 50 bar pressure in an argon atmosphere. In this example, the two slurries were applied asymmetrically to opposing sides i.e. the binder puller was applied to the side of the insert (10) and the binder pusher was applied opposite (20) to this as shown in figure 2. The HV5 iso-hardness map is shown in figure 19. It can be seen that a softer core is produced using this method, this hardness profile has been shown to provide efficient drilling behavior. The two slurries could have alternatively been applied symmetrically as shown in figure 1. By controlling the concentration and positioning of the application of the two slurries this facilitates the ability to be able to tailor the redistribution of the binder phase to meet the needs of the application.

Example 3 - Insert compression test

[0066] The toughness of drill bit inserts of samples B, C, E, F, H and I described in table 2 / example 1 were characterized using an insert compression (IC) test. The IC test method involves compressing a drill bit insert between two plane-parallel hard counter surfaces, at a constant displacement rate, until the failure of the insert. A test fixture based on the ISO 4506:2017 (E) standard "Hardmetals - Compression test" was used, with cemented carbide anvils of hardness exceeding 2000 HV, while the test method itself was adapted to toughness testing of rock drill inserts. The fixture was fitted onto an Instron 5989 test frame.

[0067] The loading axis was identical with the axis of rotational symmetry of the inserts. The counter surfaces of the fixture fulfilled the degree of parallelism required in the ISO 4506:2017 (E) standard, i.e. a maximum deviation of 0.5 μm / mm. The tested inserts were loaded at a constant rate of crosshead displacement equal to 0.6 mm / min until failure, while recording the load-displacement curve. The compliance of the test rig and test fixture was subtracted from the measured load-displacement curve before test evaluation. Three inserts were tested per sample type. The counter surfaces were inspected for damage before each test. Insert failure was defined to take place when the measured load suddenly dropped by at least 1000 N. Subsequent inspection of tested inserts confirmed that this in all cases this coincided with the occurrence of a macroscopically visible crack. The material toughness was characterized by means of the total absorbed deformation energy until fracture. The results of the insert compression test are shown in Table 3:

Table 3: Summary of Insert compression test results

Sample	Deformation energy until fracture (J)
B	7.37

(continued)

Sample	Deformation energy until fracture (J)
C	8.87
E	7.27
F	9.96
H (invention)	9.75
I (invention)	12.50

[0068] The toughness of the samples treated according to the method the present invention is higher than samples known in the prior art according to the IC test results when comparing samples that were tumbled in the same way.

Example 4- Pendulum Hammer

[0069] For the Pendulum Hammer test cemented carbide mining inserts with a dome shaped tip of 5.0 mm radius and a diameter of 10.0 mm were produced and treated in the same way samples B, C, E, F, H and I as described in example 1. A schematic drawing of the pendulum hammer test set-up is shown in figure 20. The inserts were firmly mounted into a holder (30) with only the dome section protruding. On the pendulum (40) a hard-counter surface is mounted (50) on the pendulum hammer head. The counter surface used was a polished plate (h = 5.00 mm, l = 19.40 mm, w = 19.40 mm) of a hard, fine grained hard metal grade having a Vickers hardness of approx. 1900 HV30. When the pendulum is released, the counter surface hits the sample tip. If the sample fails, the impact energy (E) absorbed by the sample measured in Joules (J) is not recorded. For a given initial pendulum angle, the impact energy is calculated using equation 3 where m is the total mass of the pendulum hammer 4.22 kg, g is the gravitational constant 9.81 m/s2, L is the pendulum hammer length 0.231 m and α is the angle in radians.

$$E= (mtot \times g \times L \times (1-\cos(\alpha)) \qquad \text{(equation 3)}$$

[0070] To determine the energy needed to fracture the sample, it is first impacted by the pendulum released from a suitable low angle. The angle is then increased step-wise with a 5 degree step until the sample fails. Following this, inserts from the same sample are impacted at a 3 degree lower angle than the impact angle that caused the failure and the test is repeated with smaller incremental increases in the impact angle. The angle where the insert does not break is recorded and the corresponding impact energy calculated. In these tests, the counter surface was exchanged every 5-10 impacts. The results are shown in table 4 below:

Table 4: Summary of Pendulum Hammer test results

Sample	Impact energy (J)
B	6.9
C	10.3
E	6.0
F	8.3
H (invention)	7.7
I (invention)	15.0

[0071] The results show that there is a significant increase in the impact resistance for the sample produced using the method of the current invention when comparing samples tumbled in the equivalent way.

Example 5 - Chemical analysis

[0072] The chemical gradient of the sample was investigated by means of wavelength dispersive spectroscopy (WDS) analysis using a Jeol JXA-8530F microprobe. Line scans along the centre line were done on cross sections of the sintered materials, prior to tumbling for samples D (comparison) and G (invention) as described in table 2 / example 1.

Samples were prepared by precision cutter, followed by mechanical grinding and polishing. The final step of the sample preparation was carried out by polishing with 1 μm diamond paste on a soft cloth. An acceleration voltage of 15kV was used to perform line scans with a step size of 100μm and a probe diameter of 100μm. Three line scans per sample were carried out and the average is reported. The cobalt concentration profiles are compared in figure 21, the chromium concentration profiles are compared in figure 22 and the Cr/Co concentration profiles are compared in figure 23.

[0073] For comparison with a cemented carbide mining insert having a higher binder concentration, line scans along the centre line were done on cross sections of sample K post tumbling. Tumbling is assumed not to affect the chemical composition nor the WDS analysis. The lines scans for the Co concentration and the Cr concentration are shown respectively in figures 24 and 25.

[0074] It can be seen that for the samples produced according to the method of this invention that the highest Co concentration can be found in the tip and the bulk of the cemented carbide insert; and the lowest Cr concentration and lowest Cr/Co concentration is found in the bulk of the cemented carbide insert.

Claims

1. A method of redistributing the binder phase of a cemented carbide mining insert comprising a WC hard-phase component, optionally one or more further hard-phase components and a binder comprising the steps of:

   a) providing a green cemented carbide mining insert;
   b) applying at least one binder puller selected from a metal oxide or a metal carbonate to the surface of the cemented carbide mining insert; and
   c) sintering the green carbide mining insert;

   characterized in that the metal oxide or metal carbonate is only applied to at least one local area on the surface of the green cemented carbide mining insert.

2. The method according to claim 1 wherein the binder puller is Cr_2O_3.

3. The method according to claim 1 or claim 2 further comprising the step between steps b) and c) of:
   applying at least one binder pusher, selected from a metal carbide, a carbon powder or a mixture thereof, to at least one different local area on the surface of the cemented carbide mining insert.

4. The method according to any of the previous claims, wherein the binder puller and the binder pusher are applied to substantially opposing local areas of the surface of the green cemented carbide mining insert.

5. The method according to any of the previous claims, wherein the binder puller and the binder pusher are applied symmetrically.

6. The method according to any of the previous claims, wherein the binder puller and binder pusher are applied asymmetrically.

7. The method according to any of the previous claims, wherein post sintering the cemented carbide mining insert is treated with a tumbling process.

8. The method according to claim 7, wherein the tumbling process is a "High Energy Tumbling" process, wherein post tumbling a homogenous cemented carbide mining insert has been deformation hardened such that $\Delta HV3\% \geq 9.72 - 0.00543 * HV3_{bulk}$.

9. A cemented carbide mining insert comprising one or more hard-phase components and a binder **characterized in that** there is a hardness gradient from a first part of the surface to a second part of the surface of the cemented carbide mining insert, wherein the first part of the surface is substantially opposing the second part of the surface, such that post sintering:

   - the first part of the surface is between 30HV3 softer and 80HV3 harder than the second part of the surface; and the first part of the surface is between 5 and 120 HV3 harder than the bulk; and
   - the second part of the surface is between 20HV3 and 70HV3 harder than the bulk

10. A cemented carbide mining insert according to claim 9, wherein
the maximum binder concentration (%binder-max) is less than 20% higher than the minimum concentration (%binder-min) within the cemented carbide mining insert.

11. A cemented carbide mining insert according to claim 9 or claim 10, wherein the %binder-min is at a depth, in percentage of the total height of the sintered cemented carbide mining insert, of between 1-50% from the first part of the surface.

12. A cemented carbide mining insert according to any of claims 9-11, wherein:

- there is a first binder concentration maximum (%binder-max1) at the first part of the surface; and
- there is a second binder concentration maximum (%binder-max2) at a depth, in percentage of the total height of the sintered cemented carbide mining insert, of between 15-75% from the first part of the surface.

13. A cemented carbide mining insert according to any of claims 9-12, wherein there is a first chromium concentration maximum (%Cr-max1) at the first part of the surface.

14. A cemented carbide mining insert according to claim 13, wherein there is additionally a second chromium concentration maximum (%Cr-max2) at the second part of the surface;

- %Cr-max1>%Cr-max2; and
- there is a chromium concentration minimum (%Cr-min) located between %Cr-max1 and %Cr-max2.

15. A cemented carbide mining insert according to claim 14, wherein the %Cr-min is at depth, in percentage of the total height of the sintered cemented carbide mining insert, of between 40-99%, from first part of the surface.

Figure 1

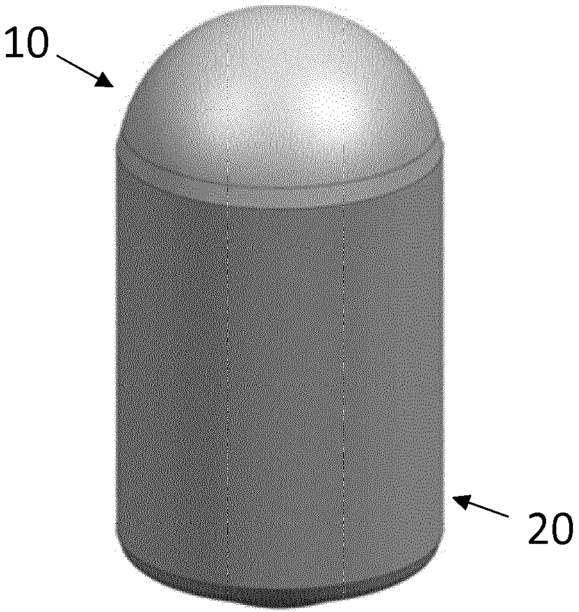

Figure 2

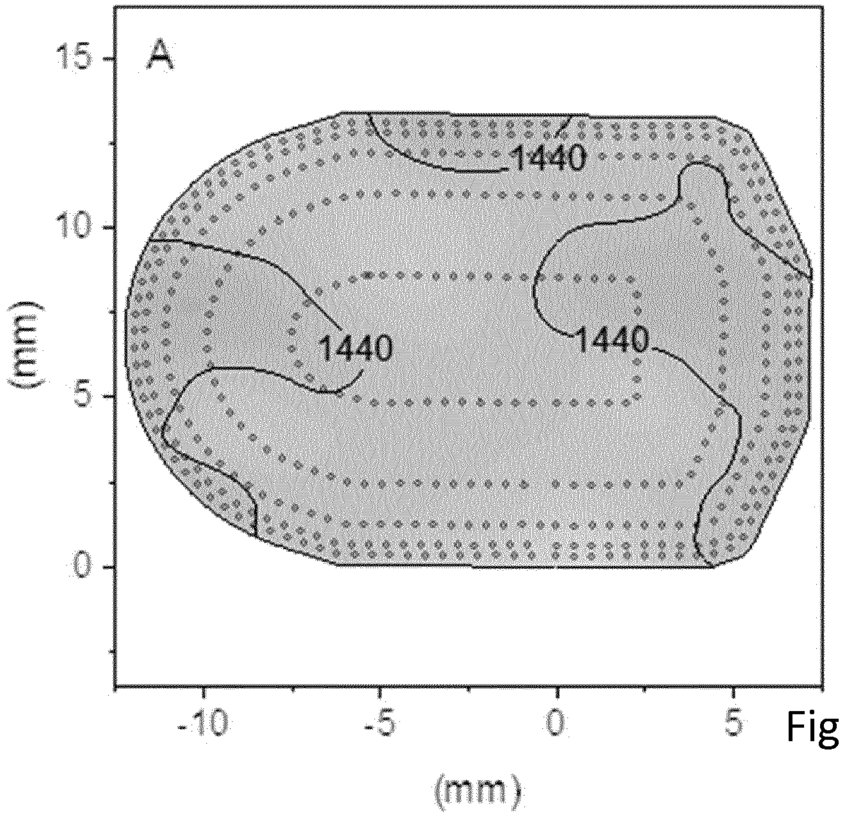

Figure 3

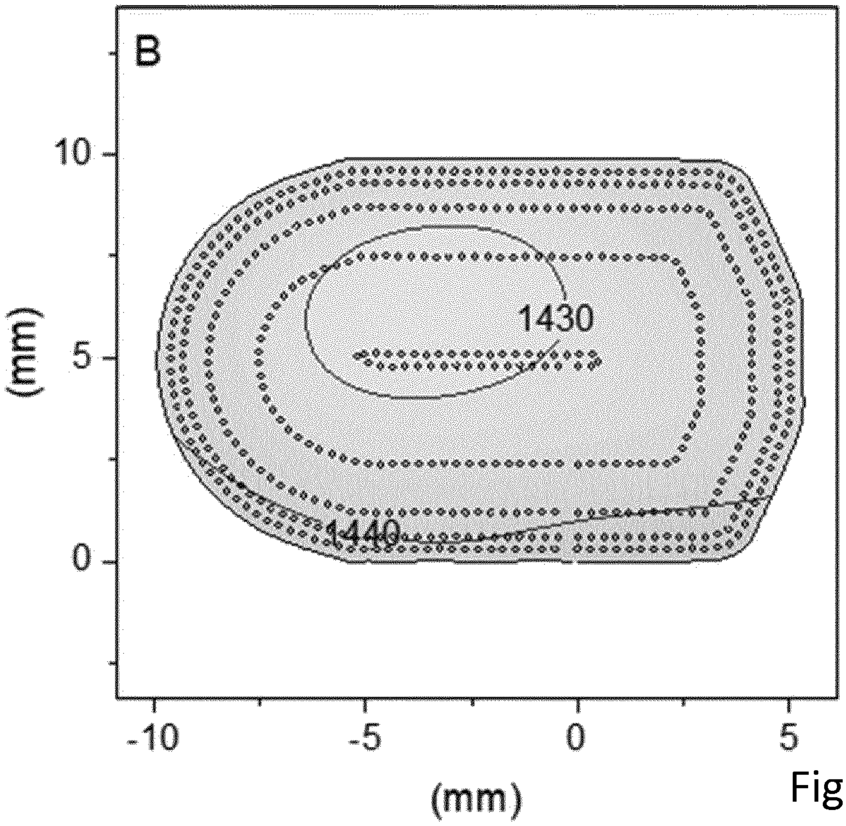

Figure 4

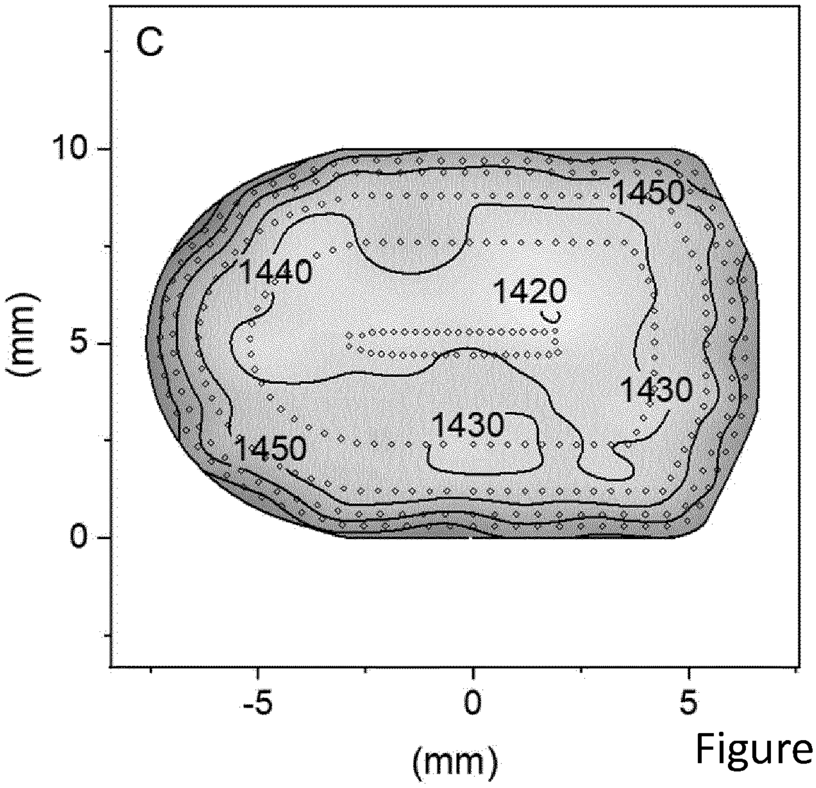

Figure 5

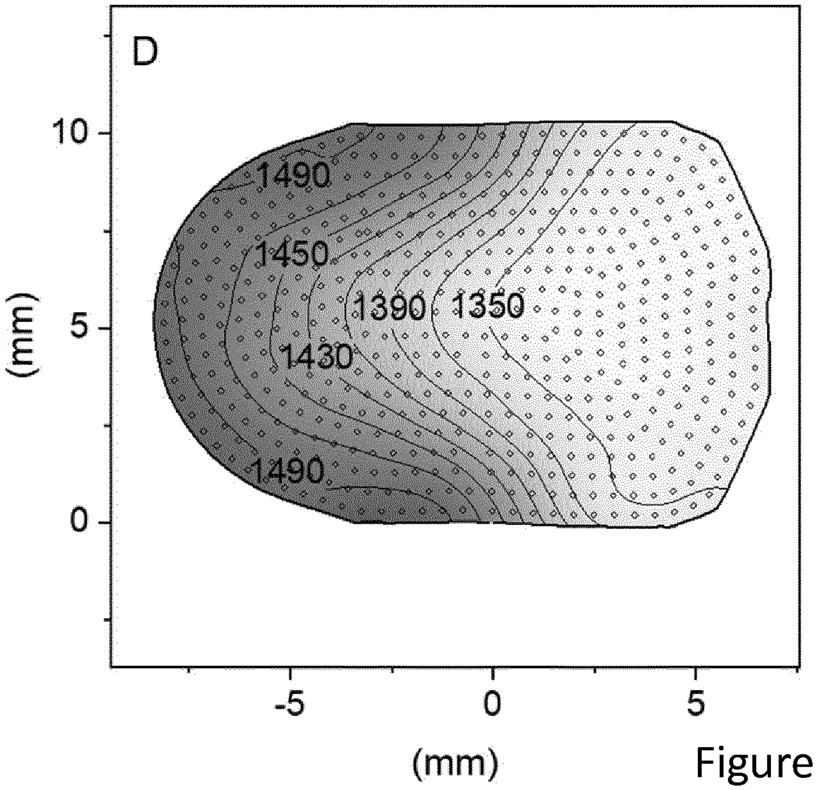

Figure 6

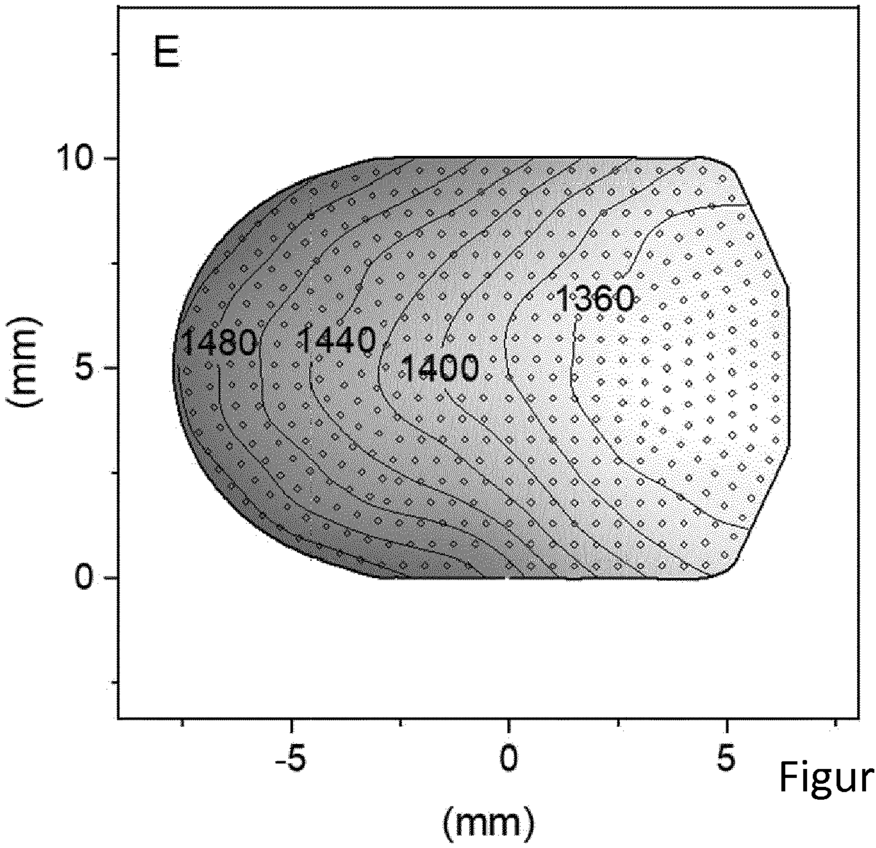

Figure 7

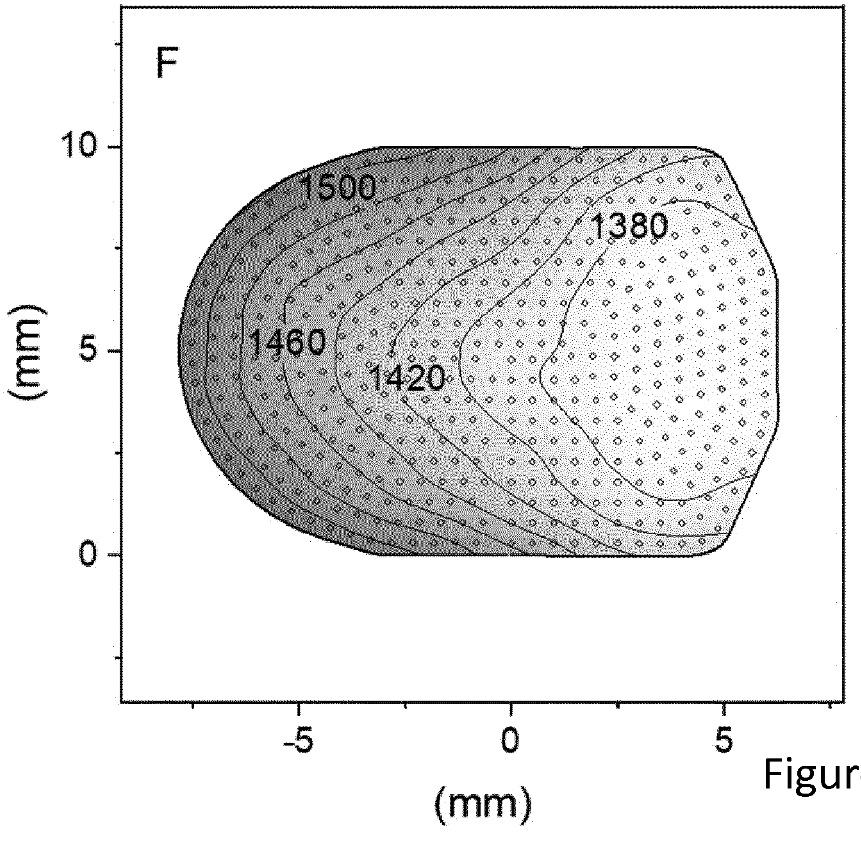

Figure 8

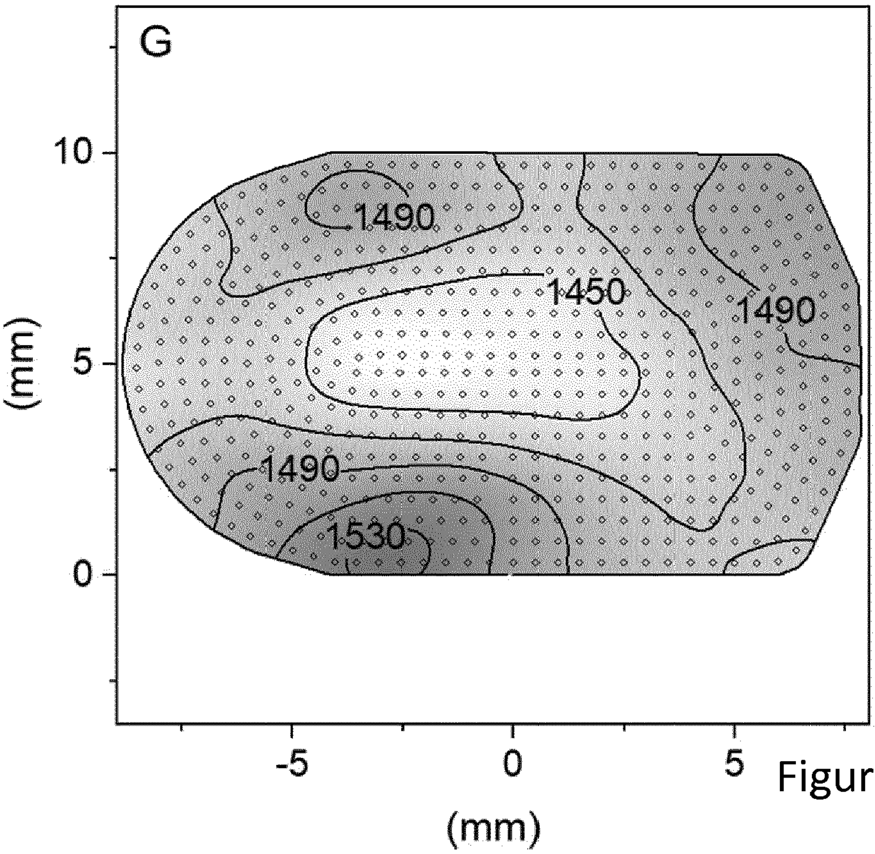

Figure 9

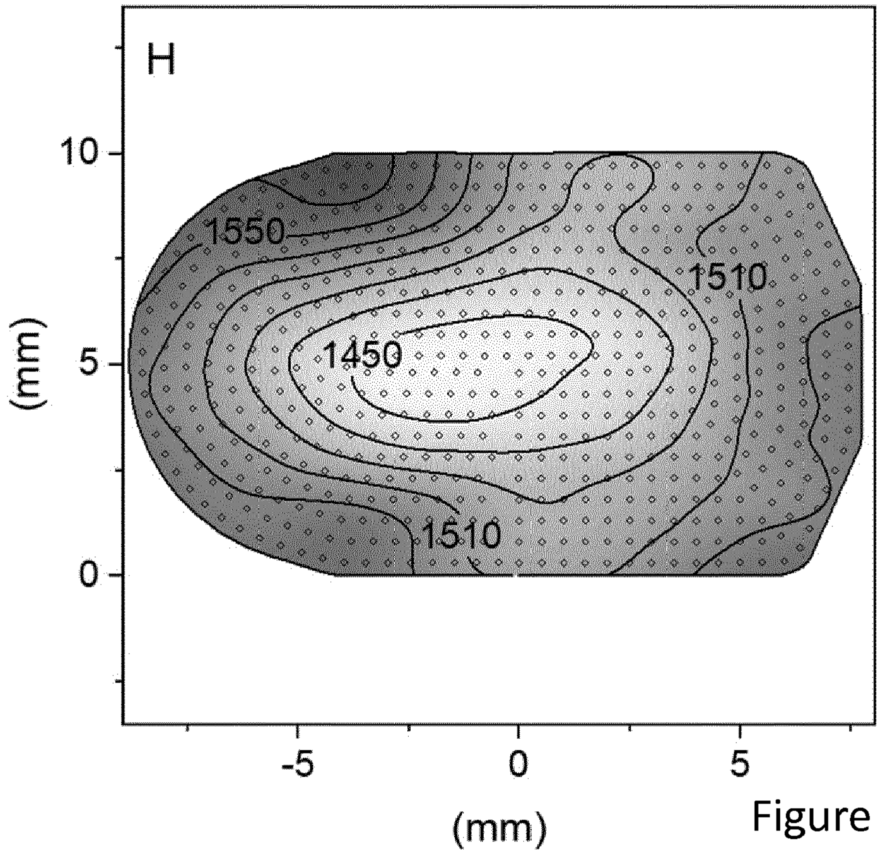

Figure 10

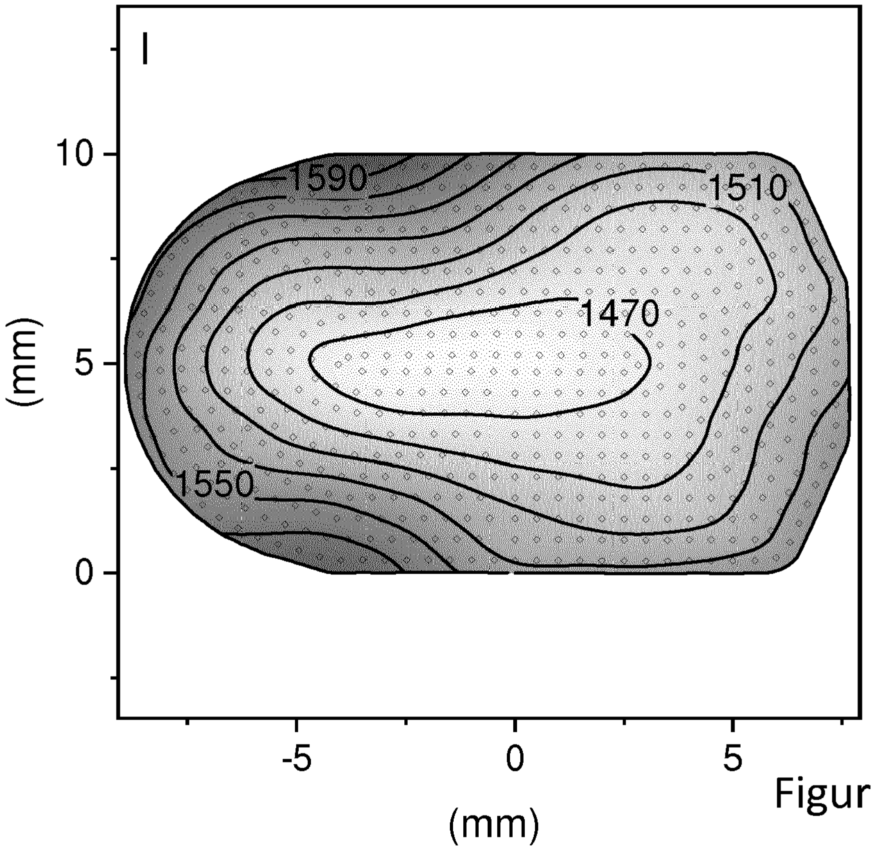

Figure 11

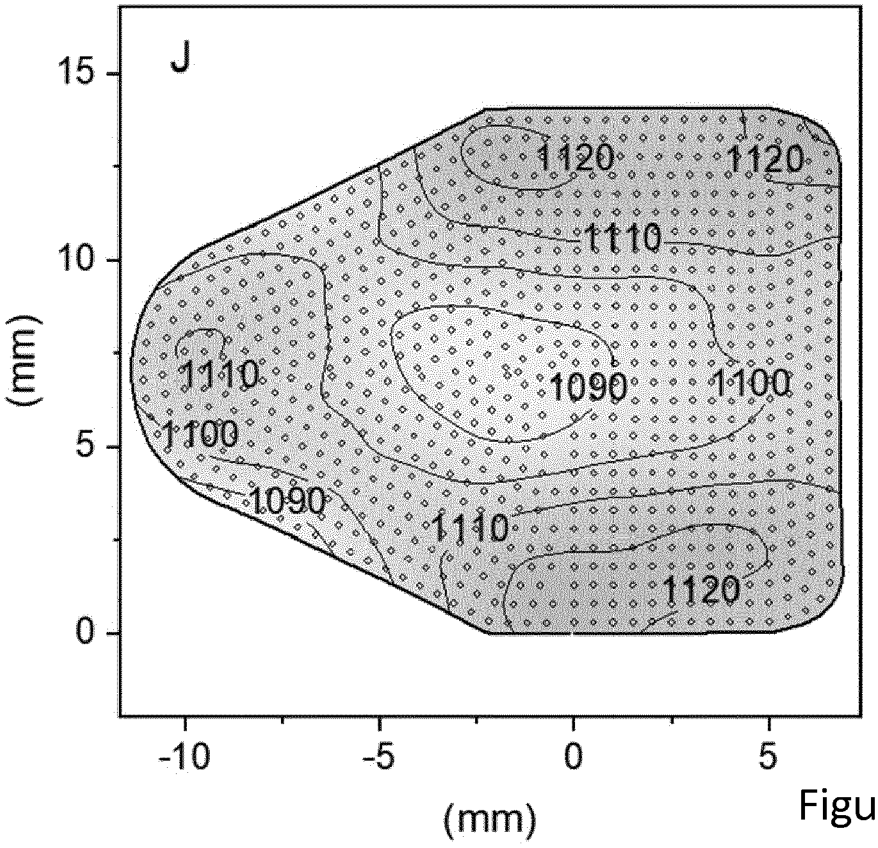

Figure 12

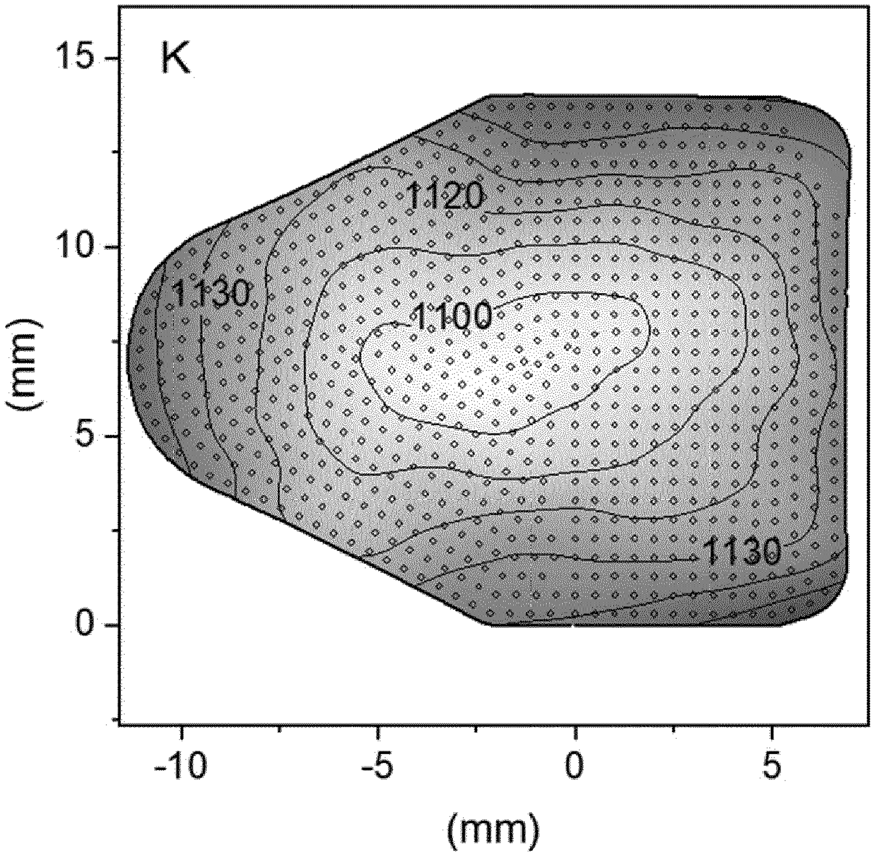

Figure 13

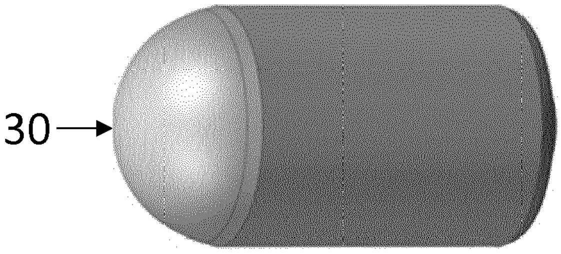

Figure 14

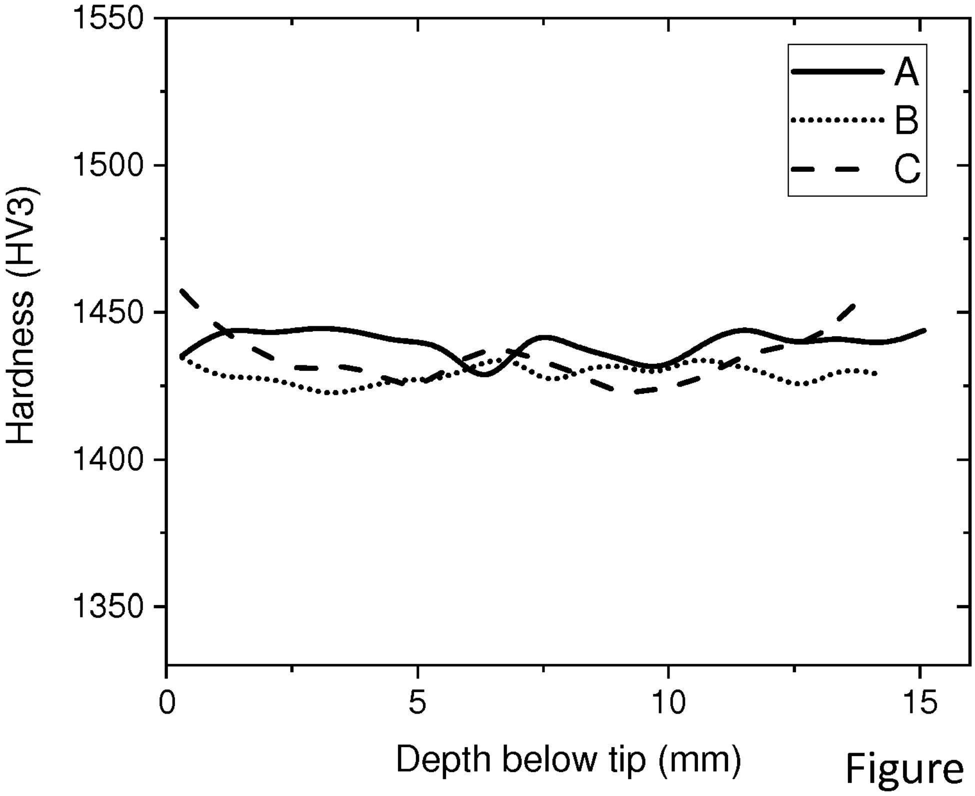

Figure 15

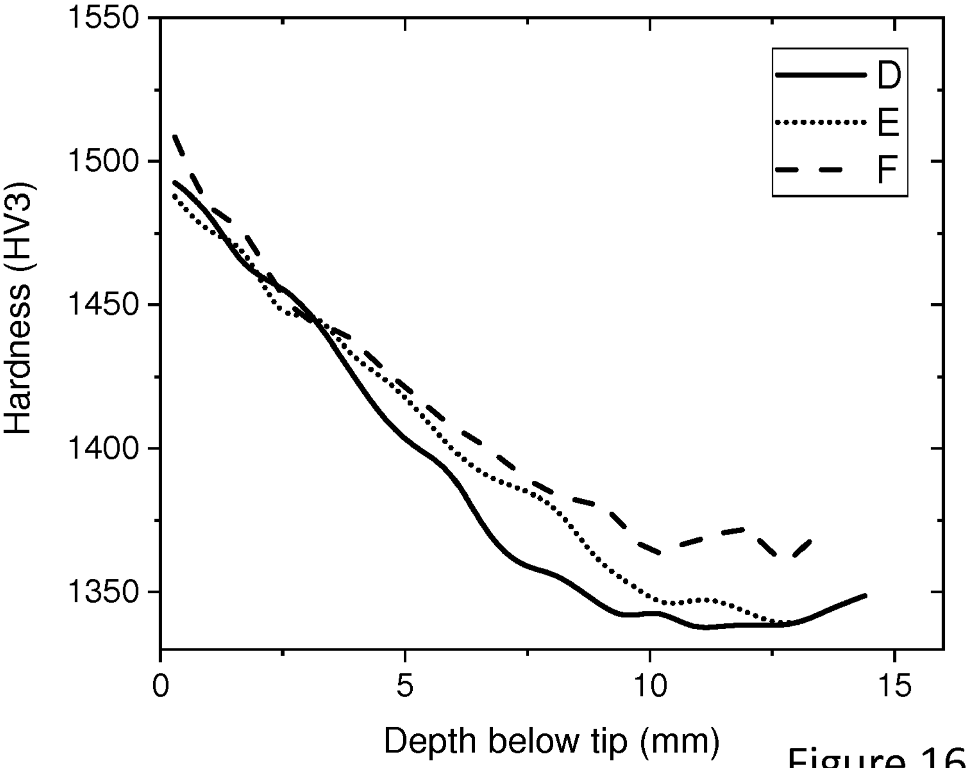

Figure 16

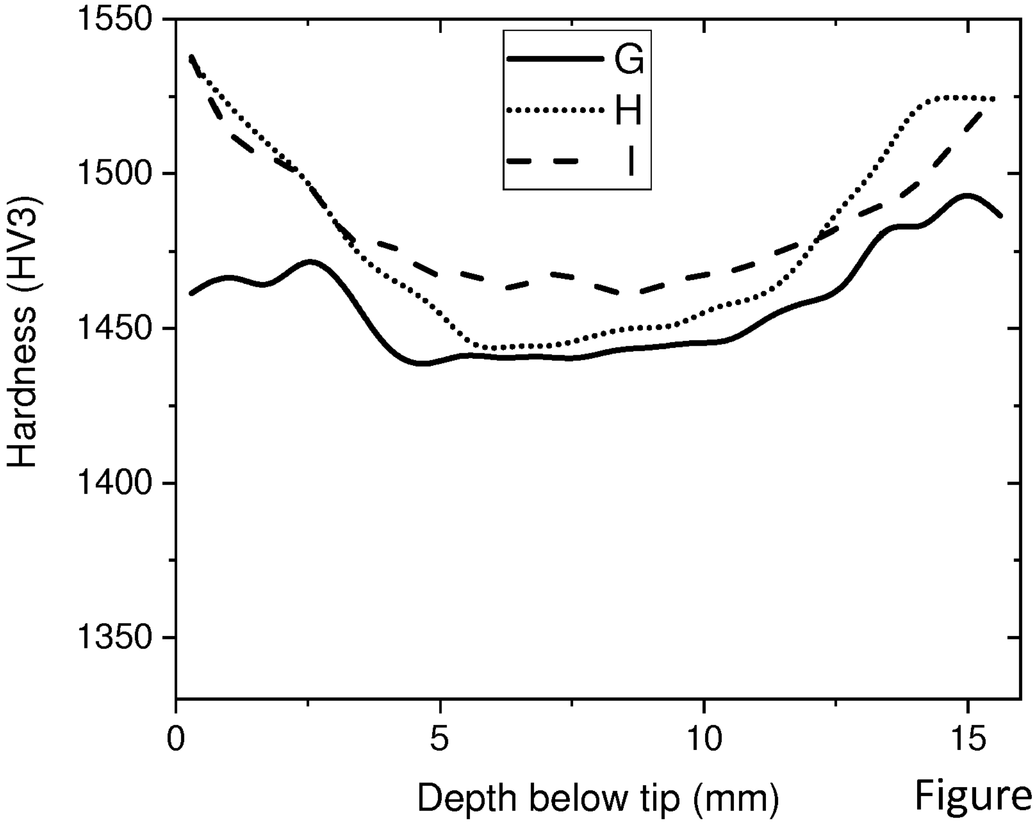

Figure 17

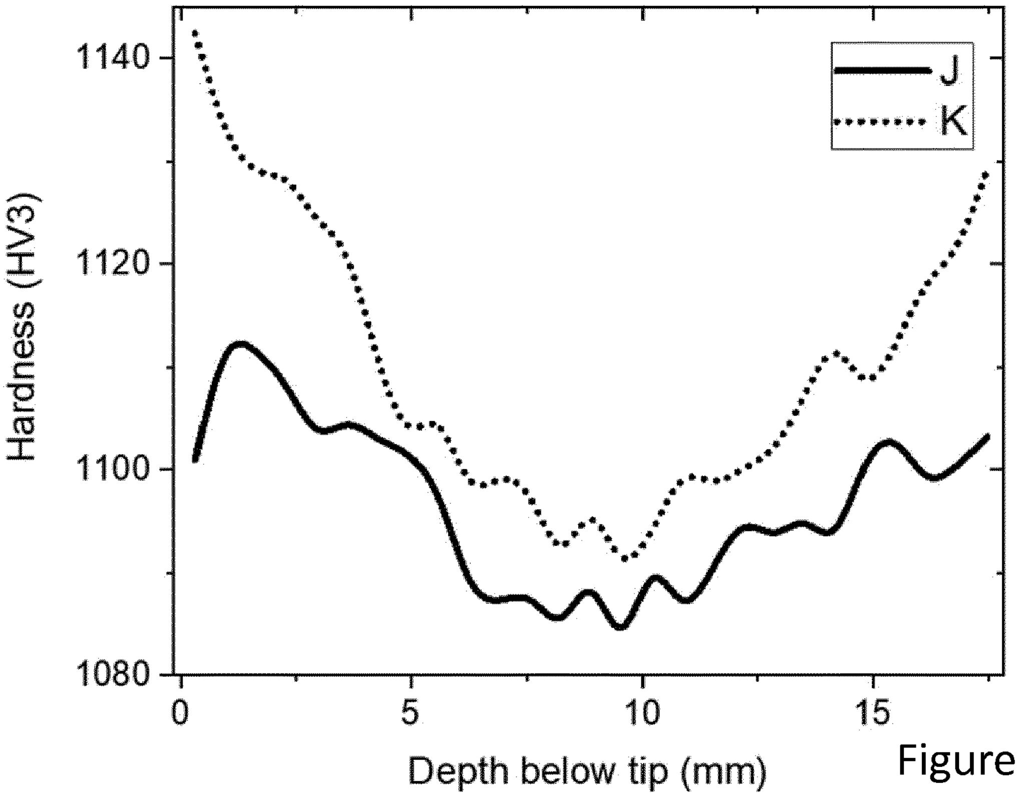

Figure 18

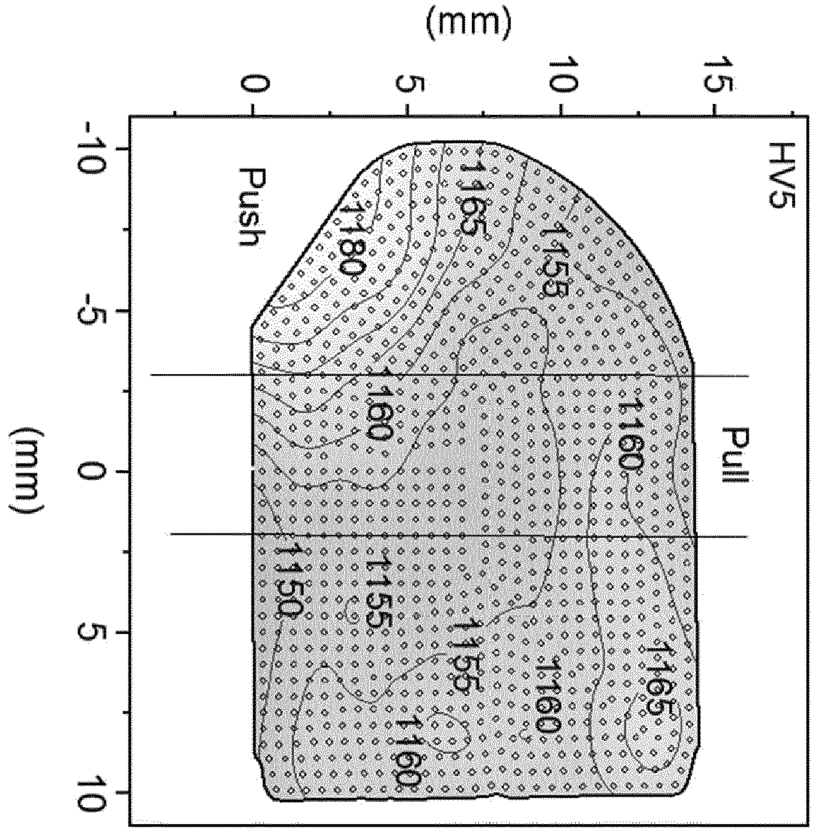

Figure 19

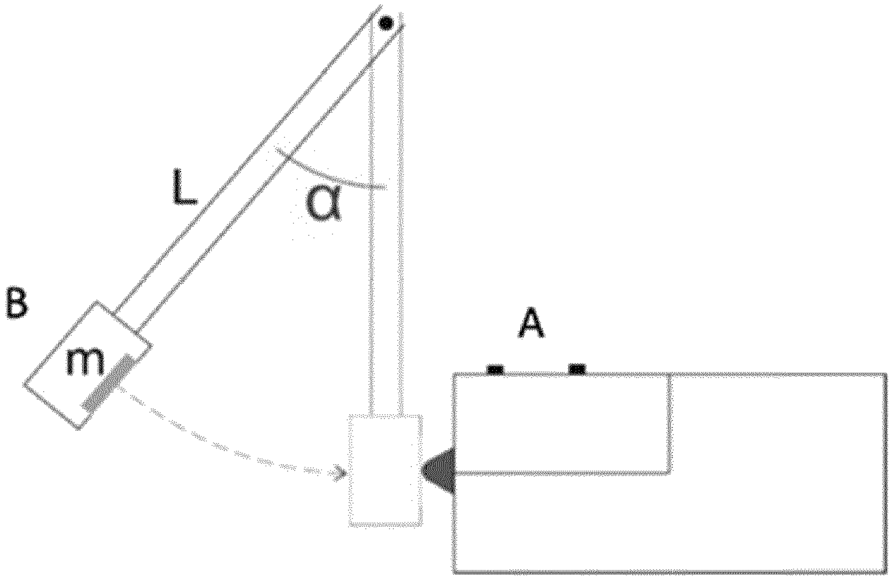

Figure 20

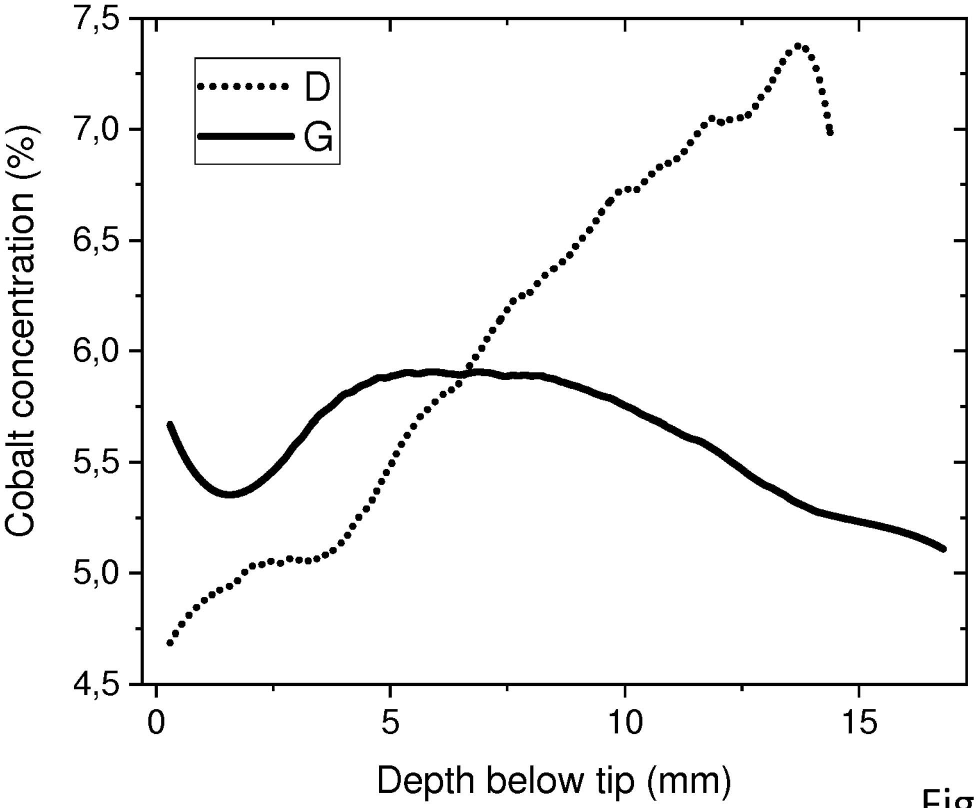

Figure 21

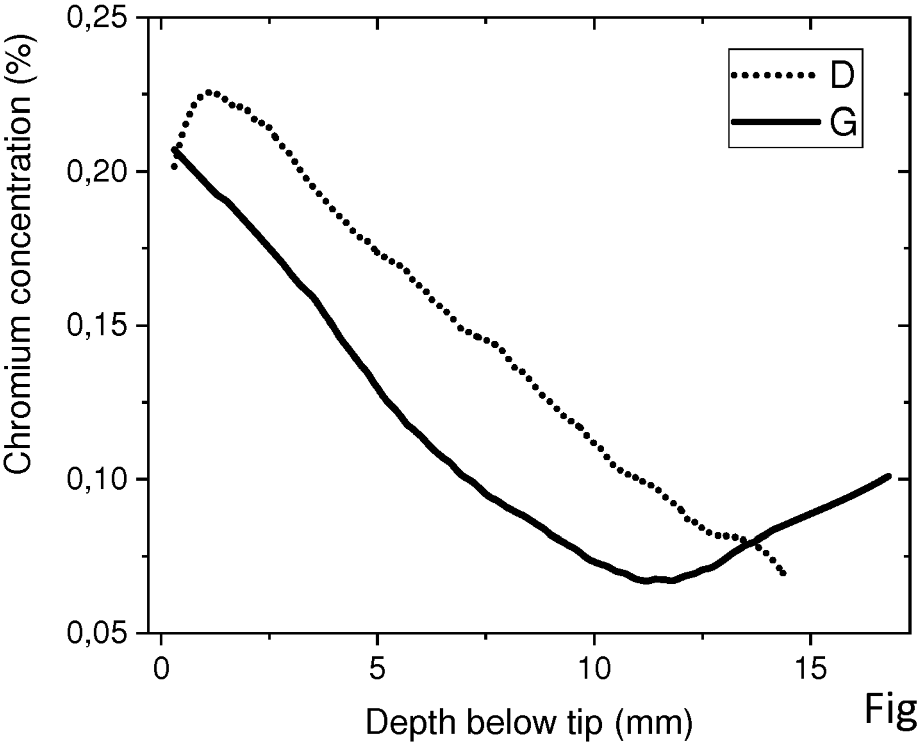

Figure 22

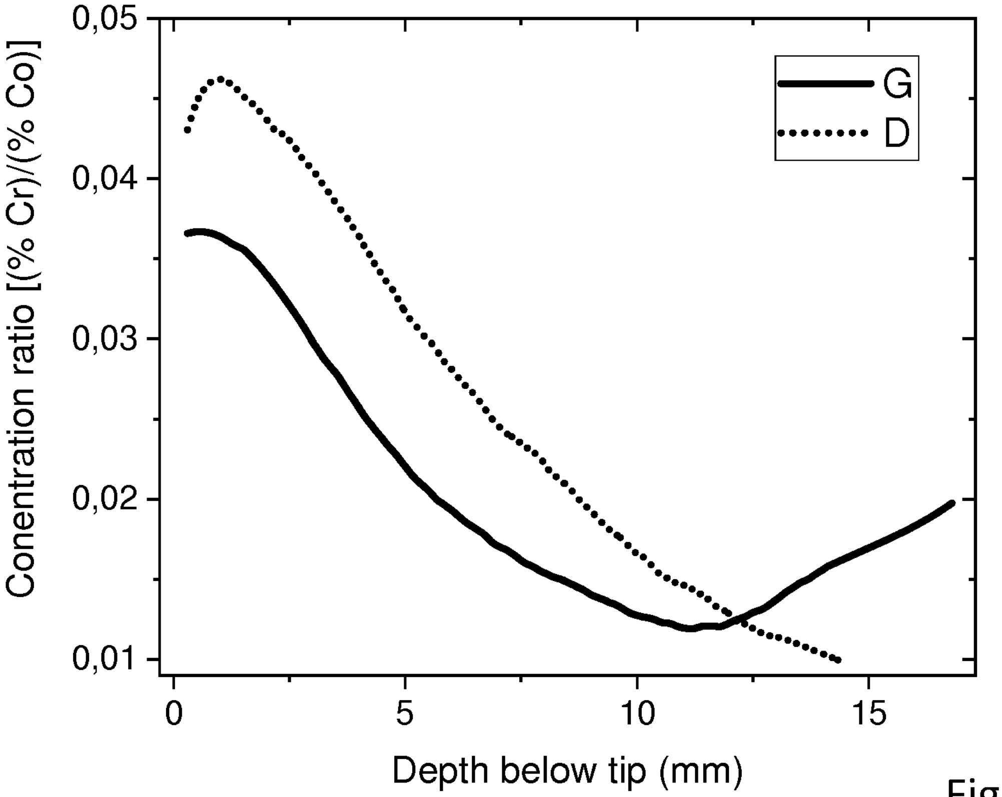

Figure 23

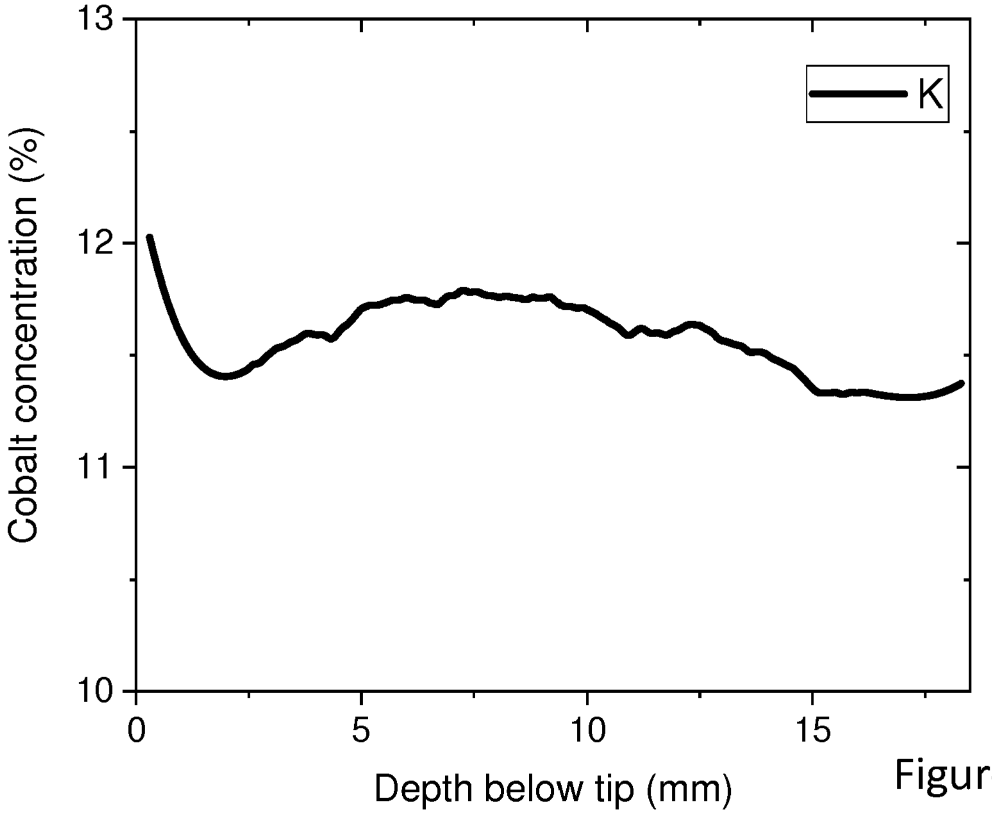

Figure 24

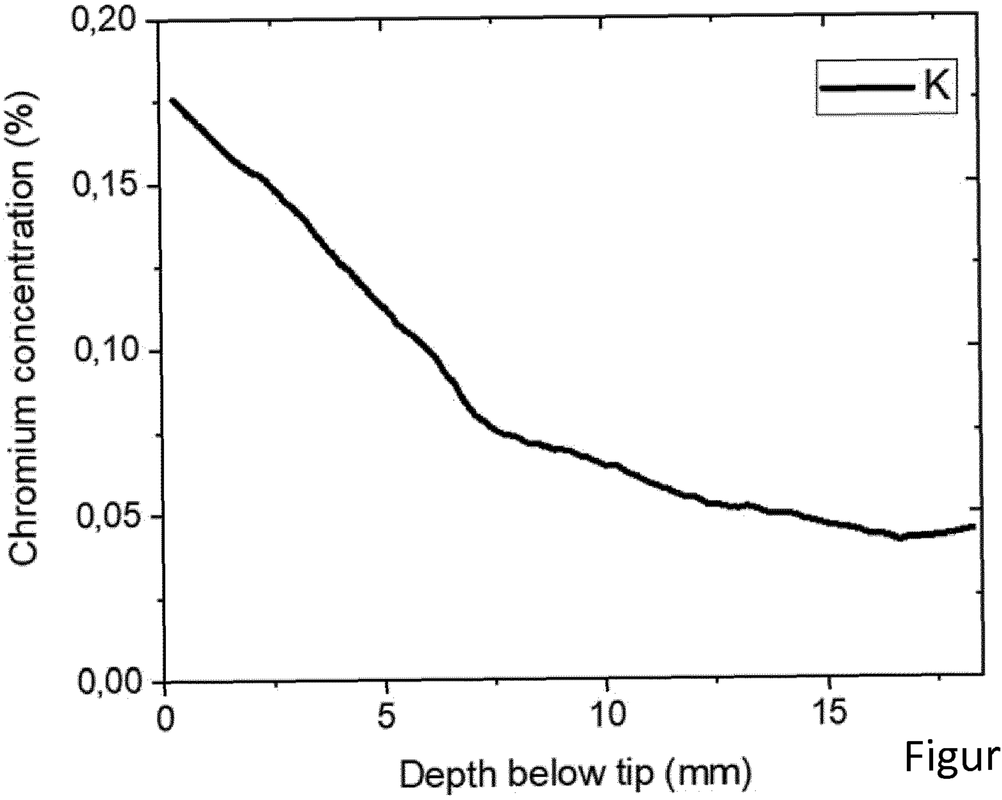
0,20
0,15
0,10
0,05
0,00
Chromium concentration (%)
0
5
10
15
Depth below tip (mm)
K

Figure 25

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 18 20 6093

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	WO 97/07251 A1 (KENNAMETAL INC [US]) 27 February 1997 (1997-02-27)	1,2,7,8	INV. C22C29/08 B22F3/24 ADD. B22F5/00
A	* claims 1, 10 * * page 3, lines 29-30 * -----	3-6,9-15	
X	WO 2018/060125 A1 (SANDVIK INTELLECTUAL PROPERTY [SE]) 5 April 2018 (2018-04-05)	9	
Y	* claim 1 *	10-15	
A	 -----	1-8	
Y	WO 2005/056854 A1 (SANDVIK AB [SE]) 23 June 2005 (2005-06-23)	10-15	
A	* claims 1, 2, 3; figures 1, 2 * -----	1-9	
A	AU 2013 273 604 B2 (SANDVIK INTELLECTUAL PROPERTY) 3 December 2015 (2015-12-03) * the whole document * -----	1-15	

TECHNICAL FIELDS SEARCHED (IPC)

C22C
B22F

The present search report has been drawn up for all claims

2

Place of search	Date of completion of the search	Examiner
The Hague	10 July 2019	Helgadóttir, Inga

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
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
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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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 18 20 6093

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