(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
22 September 2016 (22.09.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/146343 A1

(51) International Patent Classification:
B23D 61/18 (2006.01) *B23D 65/00* (2006.01)
B24B 27/06 (2006.01) *B24D 18/00* (2006.01)

(21) International Application Number:
PCT/EP2016/053626

(22) International Filing Date:
22 February 2016 (22.02.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
15158993.4 13 March 2015 (13.03.2015) EP

(71) Applicant: **NV BEKAERT SA** [BE/BE]; Bekaertstraat 2, 8550 Zwevegem (BE).

(72) Inventors: **LANGEROCK, Steven**; Molenweg 19B, 8700 Aarsele (BE). **VANHEE, Filiep**; Slagmeersenstraat 28, 8870 Izegem (BE). **HOFMAN, Luc**; Zomerstraat 32, 9800 Deinze (BE).

(74) Agent: **SEYNHAEVE, Geert**; Bekaertstraat 2, 8550 Zwevegem (BE).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

(54) **Title**: METHOD TO PRODUCE A FIXED ABRASIVE SAW WIRE WITH A METAL ALLOY FIXATION LAYER AND THE WIRE RESULTING THEREFROM

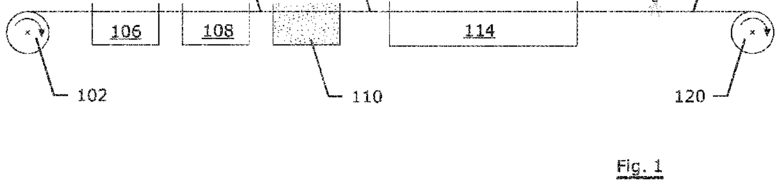

Fig. 1

(57) **Abstract**: A method is described to produce a fixed abrasive saw wire (104) by electrolytic deposition of abrasive particles pre-coated with a first metal on an elongated substrate wire (104, 202). The method is specific in that in the initial fixation bath (110) of the abrasive particles activating metal ions are added differing from the first metal. The activating metal ions deposit together with first metal ions in a fixation layer on the metallic substrate wire (104, 202) and enhance the activity of abrasive particles that are only partly coated. Thereafter a bonding layer is deposited from a deposition bath (108) that is free of added metal bonding layers. The resulting wire (104) has more than 70% of all activating metal present close to the metallic substrate wire (104, 202) within a width of 30% of the total thickness of the fixation and bonding layer

WO 2016/146343 A1

Title: Method to produce a fixed abrasive saw wire with a metal alloy fixation layer and the wire resulting therefrom.

Description

Technical Field

[0001] The invention relates to a method to produce a fixed abrasive saw wire and the fixed abrasive saw wire resulting from the method. The fixed abrasive saw wire can be used for the cutting of hard and brittle materials such as sapphire, silicon, gallium arsenide, quartz, silicon carbide, natural or manmade stone or similar materials.

Background Art

[0002] In the field of semiconductor and solar wafer manufacturing, the development of the multi-loop, single wire saw machine made the parallel cutting of several wafers (more than hundred) in one single cycle possible. In such saw machine a single length of wire is threaded in several loops over grooved capstans that keep the loops at equal distance while the workpiece is sunk into the thus formed wire web. The capstans drive the wire in forth and back movement, whereby stepwise new wire is fed at the entrance loop of the web, while used wire is extracted at the exit loop of the web.

[0003] Basically two different types of sawing processes are customary nowadays. There is the loose abrasive sawing wherein slurry containing abrasive grit – predominantly silicon carbide powder in a poly ethylene viscous carrier – is dragged by the saw wire into the cut. The sawing is done by the abrasive particles that stick and roll between the surface of the saw wire and the workpiece i.e. by means of three body abrasion. The saw wire is generally a high tensile steel wire with a smooth surface and a round cross section. Recently, improved cutting results in terms of speed and surface quality have been obtained by using micro-corrugated saw wires. In such saw wires tiny bends are made into the wire thereby improving the drag of the slurry into the cut (see WO 2014/036714A1, WO 2012/2069314 A1, both of the current applicant).

[0004] As not only the workpiece is abraded away but also the surface of the steel wire, a high replenishment rate is needed for the wire. Moreover, the slurry management adds to the complexity of the process both in terms of process control and ancillary equipment and the whole process is not environmentally friendly.

[0005] Due to this the use of fixed abrasive saw wire enjoys increased success over the past years, not only for the cutting of silicon for solar or semiconductor applications, but also for the cutting of sapphire wafers for use as blue LED substrates, camera lenses, transparent push buttons and even as smartphone screen substrates.

[0006] In a fixed abrasive saw wire the abrasive particles are fixed to the surface of the wire by means of a bonding layer. In this way the relative speed between abrasive particles and the carrier wire is zero and there is no wear of the wire i.e. the wire life is now limited by the wear life of the abrasive particles. Only a coolant is needed to remove saw swarf from the cut but this is better manageable than abrasive slurry. The bonding layer can be an organic resin bonding layer (US 6070570) or it can be a metallic bonding layer. Metallic bonding layers can be applied by brazing or soldering (WO 99/46077) or by means of electroless or electrolytic deposition (an early bird being DE 916 143). The current application concerns the latter type of fixed abrasive saw wire i.e. the holding of the abrasive particles in an electrolytically deposited metal layer.

[0007] The electrolytic co-deposition of the abrasive particles in the bonding layer is a challenge. As the abrasive particles – mostly man-made diamond grit – are electrically inert, the particles do not coat in the process. Therefore the abrasive particles are first covered with a conductive layer such as electroless Ni-P or Co-P (GB 1198479) or a semi-conductive layer like TiC or SiC (US7704127). The conductive layer need not be closed around the abrasive particle (JP2010036298A, JP2010120116A2).

[0008] Generally the deposition is a two stage process:

a. In a first ‘fixation step’, the particles are provisionally fixed to the substrate wire. Preferably, this is done in a single layer of particles without particles sticking together in clusters. This fixation is too weak to make the wire fit for sawing but needs to be strong enough to at least temporarily keep the particles to the wire during the…

b. …second ‘bonding step’ wherein the particles are bonded in position by further electrolytic deposition of a metal ‘bonding layer’. The bonding layer keeps the abrasive particles in place.

[0009] A non-exhaustive list of alternatives for the ‘fixation step’ are:

- Use of heat-meltable metal tacking layer (US2012/167482, US 2013/032129A);
- Use of an organic adhesive (JP2010/120116)
- Use of an intermediate layer that holds the particles by Van Der Waals forces (US2011/263187).
- Fixation by electroless plating (JP1271117A2).
- Fixation by electrolytic co-deposition of at least partially metal coated abrasive particles and a metal coating (e.g. WO 2011/042931A1).

In the current application the fixation step is by means of electrolytic co-deposition plating.

[0010] Problems that occur with an electrolytic fixation step are

- that particles tend to cluster prior to reaching the surface of the substrate or cluster on the substrate itself and;
- that the conductive coating on the abrasive particles dissolves in the electrolyte.

The first problem leads to unwanted, large protrusions that generate saw marks during use. The second problem leads to a decrease of abrasive particles deposition rate as the particles become electrically inert due to the dissolution of the conductive coating over time. Consequently the particles lose their ability to be fixed to the substrate wire and the particle coverage on the wire diminishes over time.

[0011] The following references have been found to be of particular relevance to the invention:

- TW2013/25780 describes a fixed abrasive saw wire comprises an ‘empty plating layer 2’ i.e. a plating layer that does not have diamond abrasive in it. Further the ‘thick layer’ is an electrodeposited layer of composition of about 70 wt% Ni and 30 wt% Co. The empty plating layer and thick layer share the same overall composition. There is no indication that the diamond particles are pre-coated. Addition of cobalt to a nickel layer is known to improve wear resistance and reduce friction.

- KR101222061B1 addresses the problem of dressing by partially coating the diamonds with nickel or cobalt or other metal by means of sputtering (i.e. the metal coating is free of phosphorous or boron) and thereafter fix them electrolytically to a metal wire. ‘Dressing’ is the action of preparing the saw wire for use by freeing the tips of the diamonds of deposited metal so that they start cutting from the first stroke. The diamonds are first fixed with a metal ’attached plating layer 220’ that is further electrolytically thickened by a ‘fastening plating layer’.
- KR20090026490A and KR20090026498A describe the manufacturing process and apparatus for a saw wire coated with diamonds. The process comprises the steps of cleaning the wire (‘washing tub 120’), putting a copper or nickel strike layer on top of it (in bath ‘130’) followed by the co-deposition of diamond and nickel in bath ‘140’, further followed by thickening up the nickel layer in bath ‘150’ to intensify the coherence of the diamonds, and ending with the deposition of a cobalt layer (bath ‘160’) to reduce the friction between the wire and the piece sawn and to increase the wear resistance of the wire.
- WO 2011/042931A1 describes a method to produce and the resulting fixed abrasive saw wire wherein the problem of dissolution of the metal pre-coating of the abrasive particle and the concomitant loss of particle deposition over time is solved by coating the outer surface of the particles with a metal that has a lower ionization tendency than silver.
- WO 2014/184457A1 describes an abrasive sawing wire wherein the abrasive particles are held in nickel-cobalt layers that are subsequently deposited one on top of the other. All layers comprise cobalt. Also a method to produce the wire is described.

Disclosure of Invention

[0012] A first object of the invention is therefore to provide a method to produce a fixed abrasive saw wire. The method solves the problems of clustering and loss of particle deposition over the lifetime of the deposition baths. A further object is to provide a fixed abrasive saw wire that is substantially free of abrasive particle clusters.

[0013] According a first aspect of the invention a method to produce a fixed abrasive saw wire is provided. The steps are as follows:

- Providing an elongated metallic substrate wire by continuously unwinding the wire from a supply spool.
- Providing abrasive particles that are at least partly covered with an alloy coating of a first metal with phosphorous or boron.
- Guiding the metallic substrate wire through a fixation bath comprising abrasive particles and ions of the first metal for electrolytically co-depositing the abrasive particles in a metal fixation layer on said metallic substrate wire. This results in an intermediate wire;
- Guiding said intermediate wire through one or more baths containing one or more bonding metal ion species for electrolytically bonding said abrasive particles in a metal bonding layer, resulting in a final wire;
- The final wire is continuously wound on a wire carrier.

The invention discriminates itself from the prior art in that the fixation bath further comprises activating metal ions that are different from the first metal ion. The activating metal ion co-deposits in the metal fixation layer and on the abrasive particles.

[0014] The metallic substrate wire can be a stainless steel filament. Stainless steel contains at least 12% Cr by weight and a substantial amount of nickel. More preferred stainless steel compositions are austenitic stainless steels as they can be drawn to fine diameters. Examples are AISI 302, AISI 301, AISI 304 and AISI 314.

[0015] Alternatively the substrate wire can be a high tensile, far drawn, plain carbon steel filament. Within the context of the invention a plain carbon steel has a minimum carbon content of 0.65%, a manganese content ranging from 0.40% to 0.70%, a silicon content ranging from 0.15% to

0.30%, a maximum sulphur content of 0.03%, a maximum phosphorus content of 0.30%, all percentages being percentages by weight. There are only traces of copper, nickel and / or chromium.

[0016] Preferably the metallic substrate wire is made of a steel core and is coated with a metal coating. Exemplary metal coatings are brass (copper zinc alloy), copper, silver, aluminium, zinc, cobalt or nickel. Particularly preferred are thicker metal coatings of alloys that have a higher electrical conductivity than stainless steel or plain steel such as copper, silver, aluminium, zinc or cobalt. A thick, better conductive metal coating makes the current flow where it is needed during deposition: at the mantle of the wire. Also particularly preferred are coatings of the first metal or of the activating metal or alloys of both metals in order to have a compatible grain growth with the fixation layer.

[0017] The cross section of the wire maybe polygonal - that offers a better surface for the abrasive particles to hold on - or round. The diameter, inclusive the metal coating if present, of the elongated metallic wire is between 60 and 300 µm, even more preferred between 60 and 120 µm, for example between 60 and 100 µm. Typical sizes are 120, 110, 100, 90, 80 or 70 µm.

[0018] The abrasive particles can be superabrasive particles such as diamond (natural or artificial), cubic boron nitride or mixtures thereof. For less demanding applications particles such as tungsten carbide (WC), silicon carbide (SiC), aluminium oxide (Al_2O_3) or silicon nitride (Si_3N_4) can be used: although they are softer, they are considerably cheaper than diamond. Most preferred is man-made diamond. For cutting sapphire the use of uncrushed diamonds having a cubo-octahedral shape has been found to be beneficial.

[0019] The size of the abrasive particles depends on the intended use and the diameter of the wire. With the size of the abrasive particles is meant the size excluding any coating provided on the particles i.e. the bare particle. For sawing of silicon for example, wire diameters between 80 µm to 120 µm are general used. The particles then have sizes between 6 to 12 µm, or 8 to 16 µm for the 80 µm wire diameter up to 12 to 15 µm for the 120 µm wire diameter.

[0020] For sawing of sapphire a somewhat larger wire diameter of between 120 μm to 180 μm is used and the particles have then sizes between 15 to 25 μm for lower diameter wires up to 35 to 45 μm for the higher wire sizes.

[0021] The limits indicate the 5% and 95% size limits of the cumulative size distribution of the particles. 90% of the abrasive particles have then a size between the mentioned limits. With the median size of the abrasive particles is meant that size wherein 50% of the particles have a lower size and 50% have a higher size. Size measurements are performed according ANSI B74.20-2004 by the ‘Low Angle Laser Light Scattering’.

[0022] The abrasive particles are at least partly covered with an alloy coating of a first metal with boron or phosphorous as intentional alloying elements. The presence of boron or phosphorous makes the coating amorphous and helps to resist the dissolution of the alloy coating in the electrolyte. The first metal is either nickel or cobalt. Most preferred is nickel. The electroless coating of the particles and in particular diamond particles with Ni-B, Ni-P, Co-P, Co-B is well-known and for example described in GB 1198479.

[0023] The initial average thickness of the alloy coating is between 20 to 800 nm, or between 50 to 200 nm. In general lower average coating thicknesses centred around about 100 nm are preferred. The average thickness of the coating is derived by double weighing wherein the mass of coating is divided to the mass of the uncoated abrasive particles. Assuming the particles to be spheroidal with a diameter equal to their measured size and taking into account the relative density of the abrasive particle and the alloy coating allows to derive an average thickness.

[0024] The mass percentage of phosphorous or boron in the total mass of the coating is larger than 6.5 % but smaller than 14%.

[0025] The abrasive particles are floating or are made to float in a fixation bath that comprises an electrolyte with ions of the first metal. Generally this will be an acidic bath comprising sulphate of the first metal, chloride of the first metal or sulphamate of the first metal or mixtures thereof, possibly complemented with boric acid as cathodic buffer or organic or inorganic brighteners.

[0026] The mass of the first metal alloy coating on the abrasive particles gradually tends to zero with the time period the abrasive particles reside in the electrolyte of the fixation bath. The abrasive particles are ‘at least partly covered’ with the alloy coating of a first metal with boron or phosphorous. With at least partly covered is also included that particles are completely covered with the alloy coating, which is the case in their initial state. During plating the alloy coating does not uniformly diminish in thickness: certain parts of the alloy coating will dissolve earlier than other parts, thereby unveiling the surface of the abrasive particles. As long as some alloy coating is present on the particle, the particle has the potentiality to be attached electrolytically to the metallic substrate wire, although this potentiality gradually weakens as the alloy coating diminishes. As abrasive particles are gradually added in order to replenish

- the ones that have been fixed to the metallic substrate wire and subsequently leave the bath and;
- the ones that are no longer electrically active

the state of coverage of any active abrasive particle will be between 100% and just above 0%.

[0027] By now adding ions of an activating metal to the fixation bath the inventors have found that the activity of the abrasive particle can be substantially prolonged. As a result the deposition of abrasive particles can be held stable over a much longer period and less abrasive particles are lost due to total dissolution of alloy coating. The activating metal co-deposits into the fixation layer. Surprisingly the inventors found also that the clustering of abrasive particles greatly diminished.

[0028] It appears– without delimiting the invention in any way by this hypothesis – that the activating metal improves the electrophoretic action of the abrasive particles by adsorbing preferentially on the partially coated abrasive particles. In other words: when some surface on the coated abrasive particles becomes free of first metal coating the activating metal becomes effective. The inventors conjecture that the activating metal ions adsorb to the freed surface and thereby maintain and improve the electrophoretic particle activity. As long as the particle is fully covered, the activating metal does not help, as the particle is already active anyhow.

[0029] This results in a better overall usage of the abrasive particles in the bath and more of the partially covered abrasive particles are co-deposited in the fixation layer compared to the situation where no activating metal is present in the fixation bath. In the latter case more abrasive particles do not get incorporated into the fixation layer and are lost.

[0030] The inventors also conjecture that as a consequence of the adsorption of the positively charged activating metal ions to the abrasive particles the abrasive particles tend to repel one another in the fixation bath. In this way the activating metal also prevents agglomeration of particles prior to deposition and therefore prevents clustering.

[0031] At the end of the useful life of the abrasive particle, i.e. when the whole first metal coating with phosphorous or boron has been dissolved away, the covering of the particle with the first metal in the fixation bath is more difficult although the activating metal still helps to move the particle to the substrate wire. However, due to the absence of a coating on the particle, the particles are held less well in the fixation layer.

[0032] The concentration of the activating metal ions in the fixation bath must not be high. Already when 0.5% of the total amount of metal ions in the bath are activating metal ions a positive effect can be observed. When starting from 100% of activating metal ions in the fixation bath, the dilution by dissolving first metal ions from the abrasive particles will diminish that concentration during use. Practically, no more than 50% of all metal ions in the fixation bath need to be activating metal ions. Even lower concentrations of the activating metal in the fixation bath as for example between 0.5 to 30% or 0.5 to 20% or even 0.5 to 10% show equally good activating behaviour of the abrasive particles. As the activating metal ion preferentially binds to the metallic substrate wire and also to the partly covered abrasive particle, the ratio of activating metal atoms on the total metal atoms of the metal fixation layer will be higher in the fixation layer than in the bath itself. The consumption of the activating metal is therefore significantly higher than the consumption of the first metal in the bath.

[0033] In a further improved embodiment of the inventive method the amount of abrasive particles that adhere to the surface of the intermediate or final wire is controlled by changing the concentration of the activating metal ion in the fixation bath. As the activating metal ions are consumed faster than the first metal ions in the bath and as the response of the abrasive particles to the presence of the activating metal ions is relatively fast, the amount of adhering particles can be steered within a reasonable time frame by increasing or decreasing the addition rate of the activating metal ions to the fixation electrolyte bath.

[0034] The amount of abrasive particles at the surface of the intermediate or final wire can be measured by using sophisticated optical monitoring techniques such as disclosed in JP2005074599A. This output can be used as an input to the addition scheme for the activating metal.

[0035] In the baths following the fixation bath the intermediate wire is coated at high efficiency with a metal bonding layer that is deposited from one or more electrolytic baths containing ions of one or more bonding metals. Distinct bonding metal ions may be present in each one of the baths. Alternatively ions of more than one bonding metal may be present in a single or more baths. The bonding layer is thicker than the fixation layer and effectively bonds the particles ‘in situ’. The bonding layer cannot become too thick as then the abrasive particles are then fully immersed in the bonding layer and do not protrude out of the surface. On the other hand if the bonding layer is too thin, it will not sufficiently hold the particle.

[0036] After deposition of the bonding layer the wire is final and is wound on a customer spool for further use.

[0037] In a preferred embodiment, not one of the bonding metal ion types in the one or more baths for depositing the bonding layer is of the activating metal ion type. In a further preferred embodiment, the one or more bonding metal ions are ions of the first metal, without any intentional presence of boron or phosphorous. The advantage is that the coating on the abrasive particles and the fixation layer are all compatible with the bonding layer and no interlayer adhesion difficulties arise. In conclusion: the bonding layer is by preference free of boron, phosphorous and the activating metal.

[0038] As a first metal and first metal ion, atoms and ions of nickel are preferred. This is by far the best metal as it is strong and tough, does not corrode and can easily deposited from an electrolytic bath.

[0039] As an activating metal one out of the group comprising cobalt, iron, manganese and tin is preferred. They all induce an increased activity of the partly covered abrasive particles. Most preferred is cobalt.

[0040] According a second aspect of the invention a fixed abrasive saw wire is described that is the outcome of the above described process. The fixed abrasive saw wire comprises a metallic substrate wire and abrasive particles. The abrasive particles are at least partly covered with an alloy coating of a first metal with phosphorous or boron. The particles are held to the substrate wire by means of fixation layer and a bonding layer on top of the fixation layer. The fixation layer comprises at least the first metal and covers the abrasive particles and the substrate wire. The fixation layer is on its turn covered with a bonding layer of bonding metal or bonding metal alloy. Both the fixation layer and the bonding layer are electrolytically deposited.

Characteristic about the wire is that the fixation layer contains, comprises an activating metal that differs from the first metal.

[0041] The types of the metallic substrate wire and the types of abrasive particles are as described in the explanation on the method. The at least partial coating of the abrasive particles with a first metal alloy with boron or phosphorous is preferably deposited by electroless deposition. The inventors consider the presence of the phosphorous and boron to be advantageous to the working of the invention as phosphorous and boron are also constituents of the electrolytic baths. By preference the first metal alloy coating with phosphorous and boron is amorphous. This to prevent any interference with magnetic fields and/or magnetic dipole interaction between particles (that could pair up and thereby form clusters). The presence of a magnetic phase can readily be ascertained by bringing the alloy coated abrasive particles in contact with a magnet: if particles are attracted, they are magnetic.

[0042] In a preferred embodiment, the bonding metal or bonding metal alloy is substantially free of the activating metal. In a further preferred embodiment the bonding metal or metal bonding alloy is the same element as the first metal. Most preferred is if the bonding metal is nickel.

[0043] The activating metal is one out of the group consisting of cobalt, iron, manganese and tin. These metals have been found particularly useful as additions to the fixation baths as they re-activate partly covered abrasive particles and thereby extend the useful life of the abrasive particles in the bath. As a consequence this activating metal can be found back into the fixation layer. The presence of the activating metal in the fixation baths results in an improved product in that there are less clusters on the surface resulting in a better sawing quality with less saw marks.

[0044] The concentration of the activating metal in the fixation layer can be between 1 and 100 wt%, between 1 and 90 wt%, or between 1 and 80 wt% of the total weight of fixation layer. The positive effects on particle distribution, i.e. less clustering, occur at very low concentration of the activating metal. Therefore, lower concentration ranges between 1 and 30% or even 1 to 20% or 1 to 10 % for example 2 to 10% of activating metal in the weight of the fixation layer already show a reduced clustering on the surface of the fixed abrasive saw wire.

[0045] With the ‘total thickness of the bonding layer and fixation layer’ or - ‘total layer thickness’ in short - is meant the thickness in radial direction as can be measured on a cross section of the saw wire in a circumferential region that is free of abrasives particles. By preference the total thickness of the bonding layer and fixation layer is related to the median size of the abrasive particles. Preferably the total layer thickness is between 25% to 75% of the median size of the abrasive particles, more preferably between 25% and 50% of the median size of the particle, such as between 25% to 33% of the median size of the particles. So for example for particles with median size of 9 μm the total layer thickness is best between 2.25 to 6.75 μm, for particles with median size 12 μm the total layer thickness is best between 3 μm and 9 μm.

[0046] In any case the fixation layer is much thinner than the bonding layer and its thickness related to the total thickness of fixation and bonding layer is less than 40 %, for example less than 30% such as less than 20%, or even less than 10%. The fixation layer is at least 1% of the total thickness of the fixation and bonding layer as otherwise the particles are not adequately held. With the fixation layer is meant that layer wherein a minimal amount of 1% or more by weight of the activating metal can be discerned in an Energy Dispersive X-ray spectroscope coupled to a scanning electron microscope (EDX-SEM).

[0047] In a preferred embodiment, the activating metal is concentrated close to the metallic substrate wire. More than 70% of all the activating metal atoms in the fixation and bonding layer are present close to the metallic substrate in the 30% of the total layer thickness of the fixation layer and bonding layer. Even more than 80% of all the activating metal atoms in the fixation and bonding layer may be present close to the metallic substrate in 20% of the total layer thickness of the fixation and bonding layer. Again this can be ascertained by making an EDX-SEM scan on a cross section of the saw wire.

[0048] The activating metal is also present around the abrasive particles. As the activating metal adsorbs to the partially coated abrasive particle it is incorporated close to the abrasive particle that is held in the fixation and bonding layer. The activating metal can also be detected in an EDX-SEM scan.

[0049] Practically the thickness of the fixation layer will be between 0.2 and 2.0 µm, for example between 0.3 and 2.0 µm or 0.3 to 1.5 µm or 0.3 to 1 µm.

[0050] In practise one strives to have between 0.1 to 1.0 grams of abrasive particles per km of wire although this may vary with the application.

Brief Description of Figures in the Drawings

[0051] Figure 1 shows the implementation of the method;

[0052] Figure 2 shows the concentration measured by EDX-SEM of

a. SEM photo: Figure 2a;
b. Nickel: Figure 2b;
c. Phosporous: Figure 2c;
d. Cobalt: Figure 2d;

[0053] Figure 3 shows the cumulative distribution of the activating metal (Co) and the first metal (Ni) throughout the coating.

Mode(s) for Carrying Out the Invention

[0054] The method will now be illustrated based on a particular example.

[0055] Figure 1 shows how the method is implemented. The installation comprises some conventional preparation steps such as unwinding a steel wire from a spool 102, cleaning the wire in an alkaline degreasing bath followed by acid cleaning 106. Optionally the wire can be pre-coated with a metallic flash coating in bath 108. These optional steps are known to the skilled person. The resulting wire 104 is the elongated metallic substrate wire that is the starting product for the method. The steel wire is a 120 µm plain carbon (0.80 wt% carbon) steel wire with a tensile strength of about 3950 N/mm² coated with brass. Prior to deposition of abrasive particles, the wire is coated with a 700 nm layer of nickel to have a compatible surface in the fixation bath.

[0056] The substrate wire 104 is led into fixation bath 110 that comprises:

a. Abrasive particles that are at least partly covered with an alloy coating of a first metal with phosphorous or boron. In this particular case the abrasive particles are crushed and size selected man-made diamond grit of a size range 12 to 15 µm. They are coated with a nickel phosphorous coating wherein the ratio coating to diamond weight was 18% by weight. The concentration of phosphorous in the nickel alloy coating was 10 wt% taken to the total of the coating. The concentration of the diamond particles in the fixation bath correlates with the amount of particles one wants to deposit on the wire.

b. The abrasive particles are floating or are made to float in an electrolyte that predominantly contains metal ions of the first metal in this case nickel. A typical mix of nickel deposition bath is:

Nikkelsulfamate electrolyte	**Amount (unit)**
Ni sulfamate ($Ni(SO_3NH_2)_2 \cdot 4H_2O$)	440 g/l
$NiCl_2 \cdot 6H_2O$	20 g/l
H_3BO_3	30-40 g/l
pH	3,2 - 3,80
Temperature	45°C

c. To this bath a minor amount of about 20 g/l of $CoCl_2 \cdot 6H_2O$ salt is added. The salt is well compatible with the other constituents of the bath and a concentration of about 5 g/l of Co^{2+} and 85 g/l of Ni^{2+} or 5.6 wt% of Co^{2+} on the total concentration of cobalt and nickel is obtained. Cobalt acts in this embodiment as activating metal.

[0057] Upon exit of the fixation bath the surface of this intermediate wire is dotted with diamond particles that only very lightly adhere to the surface. In the subsequent bonding bath 114 the wire and abrasive particles are conformably coated with a thicker layer of bonding metal or bonding metal alloy. For convenience nickel is used to this end. The number of baths, current densities, concentrations etc… are known to the skilled person and are used to tune the thickness of the bonding layer.

[0058] Although the method is described in a horizontal fashion i.e. the movement of the wire is horizontal, it is not excluded that in certain parts of the installation the wires runs approximately vertical.

[0059] In Figure 2 the elemental distribution obtained by EDX-SEM technique illustrate where the active metal actually arrives in a cross section of the wire. Figure 2a is a SEM picture of the area of interest. Figure 2b shows the distribution of nickel in a cross section through a diamond particle 204 and the substrate wire 202. The nickel layer 204 completely and conformably encloses the diamond particle. Figure 2c shows the distribution of phosphorous that is only found in the vicinity of the diamond particle. The coating is less than 1 µm thin. Figure 2d shows the distribution of the activating metal cobalt. The cobalt is predominantly present in a thin surface layer less than 1 µm thick on the surface of the wire. Outside that an even thinner layer of cobalt is discernible on the surface of the abrasive particle. It is this layer that activates the abrasive particle and improves the active life of the abrasive particle.

[0060] Figure 3 illustrates that most of the cobalt – the activating metal – deposits in the close vicinity of the metallic substrate wire. Here the ‘relative cumulative counts (RCC)’ are detected along a line perpendicular to the surface of the substrate wire. The number of counts is proportional to the amount of cobalt atoms detected. The distance to the substrate wire is indicated with T (in µm). The cumulative sum is taken outwardly starting from the surface of the substrate wire and afterward divided by the total number of counts and expressed in a percentage. Also the amount of nickel counts is cumulatively expressed in the same graph (the dashed line).

[0061] At about 5.11 µm no more nickel atoms are detected and the nickel curve flattens. The total coating is therefore about 5.11 µm thick. At about 1 µm already 90% of all cobalt atoms have been counted. So more than 90% of all cobalt is present within a layer of 1 µm i.e. within 19.6 % of the layer thickness. Hence the cobalt layer is extremely thin. The two limiting cases wherein more than 80% of all cobalt atoms can be found within a layer of 20% of the total coating thickness above the substate wire (L 80/20) and wherein more than 70% of all cobalt atoms can be found within a layer of 30% of the total coating thickness are also indicated. Note that the trace must be taken over a line that does not include a diamond particle, where also some cobalt is present.

[0062] When running the method in the absence of cobalt in the fixation bath, the diamond deposition goes through a strong active peak where a lot of diamond is deposited followed by a strong decrease in deposition efficiency to zero as the coating on the abrasive particles is corroded away. This leads to a difficult to control diamond deposition with clusters and uneven deposition of diamond particles over the length of the wire. When using the inventive method the deposition starts also with an active peak put the fall off is much longer and decreases slower than in the prior art process. As a result the deposition of diamond over length is much more uniform and less clusters are observed.

Claims

1. Method to produce a fixed abrasive saw wire comprising the following steps:
    - continuously unwinding an elongated metallic substrate wire;
    - providing abrasive particles at least partly covered with an alloy coating of a first metal with phosphorous or boron;
    - guiding said metallic substrate wire through a fixation bath comprising said abrasive particles and ions of said first metal for electrolytically co-depositing said abrasive particles in a metal fixation layer on said metallic substrate wire resulting in an intermediate wire
    - guiding said intermediate wire through one or more baths containing ions of one or more bonding metals for electrolytically bonding said abrasive particles in a metal bonding layer, resulting in a final wire;
    - continuously winding said final wire on a wire carrier;

    characterized in that

    said fixation bath further comprises ions of an activating metal, said activating metal differing from said first metal ion, said activating metal ions co-depositing in said metal fixation layer and on said abrasive particles, said activating metal ions for activating the surface of said at least partly covered abrasive particles and wherein each of said one or more bonding metal ions is different from said activating metal ion.

2. The method according to claim 1, wherein said one or more bonding metal ions are first metal ions.

3. The method according to any one of claims 1 to 2 wherein said first metal ion is nickel.

4. The method according to any one of claims 1 to 3 wherein said activating metal is one out of the group consisting of cobalt, tin, manganese and iron.

5. The method according to any one of claims 1 to 4 wherein the concentration of activating metal ions is higher than 0.5 % and less than 100 % of the total number of metal ions in said fixation bath.

6. The method according to any one of claims 1 to 5 wherein the amount of abrasive particles present on the surface of the intermediate or final wire is controlled by changing the concentration of the activating metal ions in said fixation bath.

7. A fixed abrasive saw wire comprising a metallic substrate wire and abrasive particles, said abrasive particles being at least partly covered with an alloy coating of a first metal with phosphorous or boron, said abrasive particles being held to said metallic substrate wire by a fixation layer comprising said first metal, said fixation layer covering said abrasive particles and said substrate wire, said fixation layer further being covered by a bonding layer of a bonding metal or bonding metal alloy, said fixation layer and bonding layer being electrolytically deposited,
characterized in that
said fixation layer further comprises an activating metal, differing from said first metal and wherein said bonding metal or bonding metal alloy is substantially free of said activating metal.

8. The fixed abrasive saw wire according to claim 7 wherein said bonding metal or bonding metal alloy is equal to said first metal.

9. The fixed abrasive saw wire according to claim 8 wherein said first metal, said bonding metal or bonding metal alloy is nickel.

10. The fixed abrasive saw wire according to any one of claims 7 to 9 wherein said activating metal is one out of the group consisting of cobalt, tin, manganese and iron.

11. The fixed abrasive saw wire according to any one of claims 7 to 10 wherein the concentration by weight of said activating metal in said fixation layer is between 1 and 90 % of the total weight of metals in said fixation layer.

12. The fixed abrasive saw wire according to any one of claims 7 to 11 wherein the total thickness of said fixation layer and said bonding layer is between 25 and 75 % of the median size of the abrasive particles.

13. The fixed abrasive saw wire according to any one of claims 7 to 12 wherein the thickness of the fixation layer is less than 40 % of the total thickness of the fixation layer and bonding layer.

14. The fixed abrasive saw wire according to any one of claims 7 to 13 wherein more than 70% of said activating metal atoms is present close to said metallic substrate wire within 30% of the total thickness of the fixation layer and bonding layer.

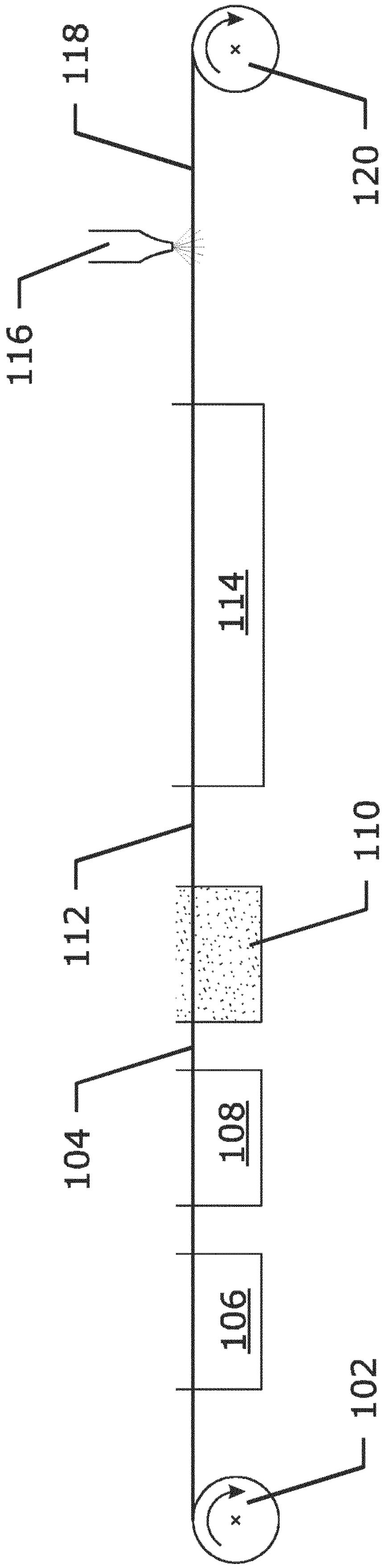

Fig. 1

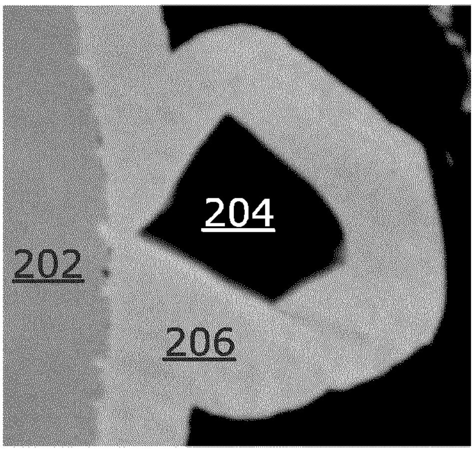

Fig. 2a

Fig. 2b

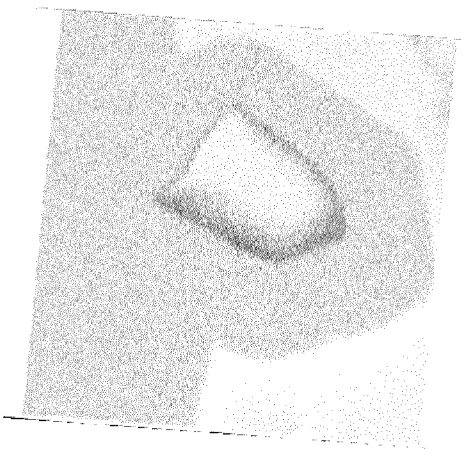

Fig. 2c

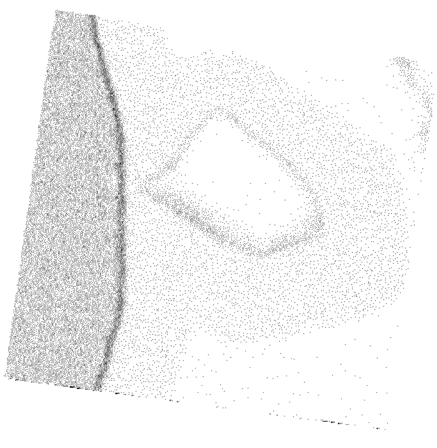

Fig. 2d

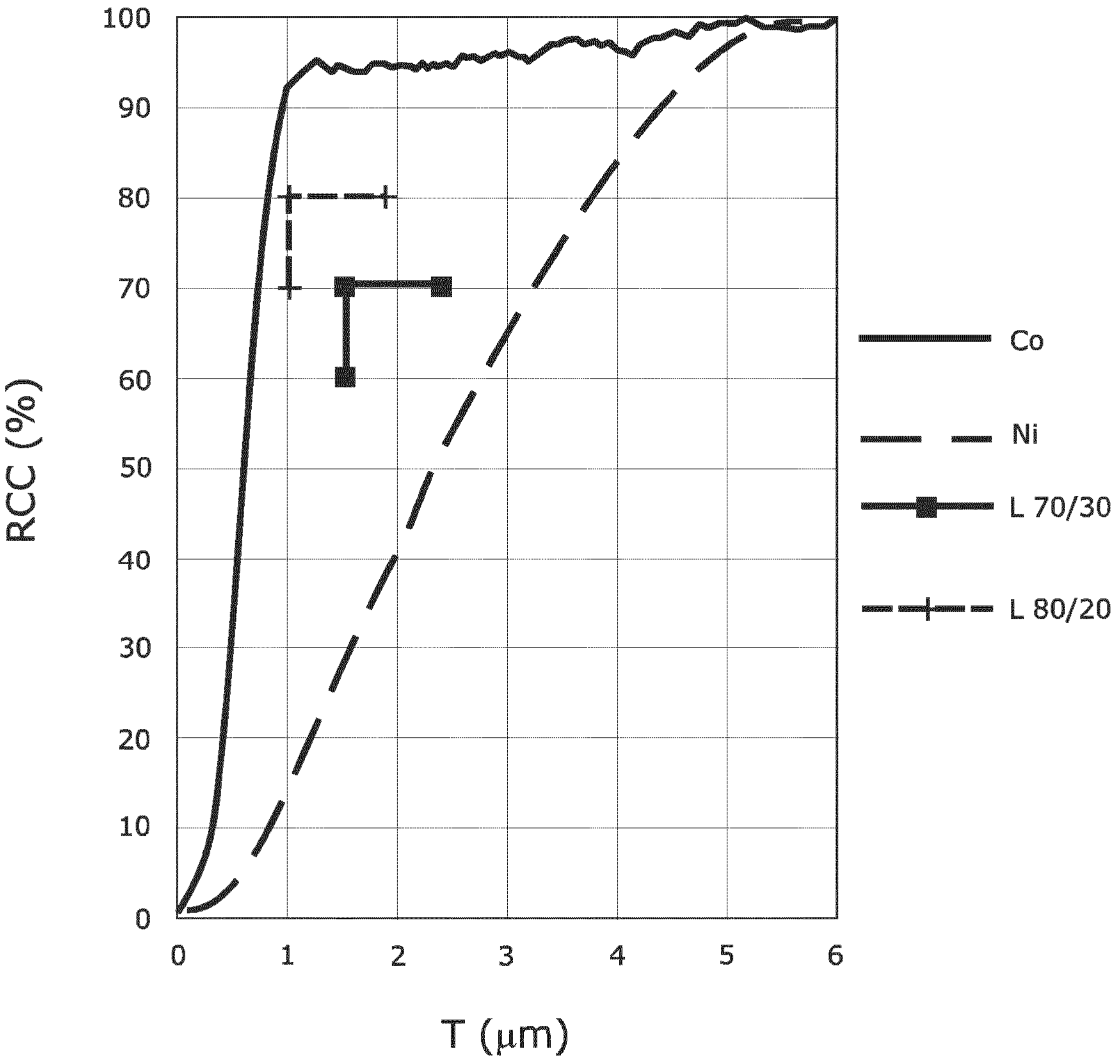

Fig. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/053626

A. CLASSIFICATION OF SUBJECT MATTER
INV. B23D61/18 B24B27/06 B23D65/00 B24D18/00
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B23D B24B B24D

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	WO 2014/006119 A1 (BEKAERT SA NV [BE]) 9 January 2014 (2014-01-09) paragraphs [0001], [0033], [0040], [0043], [0045], [0050] - [0052], [0064] page 18, lines 6-16 claims 7,9,10 figures 2-4 -----	1-4,7, 10,13 5,6,8, 11,12,14
A	WO 2014/063910 A1 (BEKAERT SA NV [BE]) 1 May 2014 (2014-05-01) paragraphs [0001], [0021], [0026], [0028], [0034], [0067] figures -----	1,7
A	KR 2009 0026498 A (KIM JUNG MUK [KR]) 13 March 2009 (2009-03-13) cited in the application paragraphs [0014], [0038], [0060] - [0063] -----	1,7

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 April 2016	20/04/2016

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Chariot, David

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2016/053626

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2014006119 A1	09-01-2014	CN 104411436 A	11-03-2015
		JP 2015521957 A	03-08-2015
		TW 201420737 A	01-06-2014
		US 2015144120 A1	28-05-2015
		WO 2014006119 A1	09-01-2014
WO 2014063910 A1	01-05-2014	NONE	
KR 20090026498 A	13-03-2009	NONE	