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(71) Applicant (for all designated States except US): **ELEMENT SIX LTD** [IE/IE]; Shannon Industrial Estate, Shannon, County Clare (IE).

(71) Applicant (for MW only): **DONALD, Heather June** [ZA/ZA]; P.o Box 454, 0001 Pretoria (ZA).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **O'GRADY, Adam Derick** [IE/IE]; Shannon Industrial Estate, Shannon, County Clare (IE). **ROSS, Michael Joseph Smyth** [IE/IE]; Shannon Airport Estate, Shannon, County Clare (IE). **REDMOND, James Martin** [IE/IE]; Shannon Industrial Estate, Shannon, County Clare (IE).

(74) Agents: **SPOOR & FISHER** et al.; P O Box 454, 0001 Pretoria (ZA).

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(54) Title: METHOD OF TREATING A DIAMOND CONTAINING BODY

(57) Abstract: The invention provides for a method of treating a diamond containing body having at least one metal dispersed through its microstructure. The metal is in the form of an anodic metal having a standard reduction potential E°_{red} (anodic). The method includes the step of treating the diamond containing body in order to remove some or all of the metal from the diamond containing body. The treating step includes contacting the diamond containing body with a solution containing metal cations having a standard reduction potential E°_{red} (cathodic), the metal cations being selected such that E°_{red} (cathodic) - E°_{red} (anodic) is greater than zero.



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METHOD OF TREATING A DIAMOND CONTAINING BODY

BACKGROUND OF THE INVENTION

This invention relates to a method of treating a diamond containing body such as, for example, a diamond (PCD) compact or non-diamond intergrown compact.

Cutting and abrading tool components utilising diamond compacts are used extensively in drilling, milling, cutting, bearings, seals and other such abrasive applications. In the case of PCD compacts, the tool component will generally comprise a layer of PCD bonded to a support, generally a cemented carbide support. In the case of non-intergrown diamond compacts, these are typically in the form of a layer of diamond grains bound in a metal matrix, which may also be bonded to a suitable support or may be free standing. The diamond compacts may present a sharp cutting edge, point, cutting or abrasive surface, bearing, seal or other wear part.

PCD compacts typically comprise a mass of diamond particles containing a substantial amount of direct diamond-to-diamond bonding. Polycrystalline diamond will typically have a second phase containing a transition metal such as cobalt, nickel, iron or an alloy containing one or more such metals.

Non-intergrown diamond compacts also typically contain one or more metals or metal alloys, which typically function as a binder for the diamond grains. Whether in the form of a PCD compact or a non-intergrown diamond compact, the diamond containing bodies to be treated incorporate one or more metals in their microstructure, which metals may or may not be residual and as such may or may not have been a solvent/catalyst, infiltrant, binder or sintering aid between sintered or unsintered diamond grains.

In use, a cutting tool component or insert comprising a PCD compact is subjected to heavy loads and high temperatures at various stages of its life. In the early stages of subterranean drilling, for example, when the sharp cutting edge of the insert contacts the subterranean formation, the cutting tool is subjected to large contact pressures. This results in the possibility of a number of fracture processes such as fatigue cracking being initiated.

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As the cutting edge of the insert wears, the contact area increases and contact stress becomes generally too low to cause high energy failures. However, this stress can still propagate cracks initiated under high contact pressures and can eventually result in spalling-type failures. As the contact area increases, the frictional process generates increasing amounts of heat.

In optimising cutter performance, increased wear resistance (in order to achieve better cutter life) is typically achieved by manipulating variables such as average abrasive grain size, overall transition metal content, abrasive density and the like. Typically, however, as a PCD material is made more wear resistant it becomes more brittle or prone to fracture. PCD elements designed for improved wear performance will therefore tend to have poor impact strength or reduced resistance to spalling. This trade-off between the properties of impact resistance and wear resistance makes designing optimised structures, particularly for demanding applications, inherently self-limiting.

If the chipping behaviours of more wear resistant PCD can be eliminated or controlled, then the potentially improved performance of these types of cutters can be more fully realised.

It is known that removing all the transition metal from a layer of PCD results in substantially improved resistance to thermal degradation at high temperatures, as disclosed in US 4,224,380 and GB 1 598 837. JP 59219500 claims an improvement in the performance of PCD sintered materials after a chemical treatment of the working surface. This treatment dissolves and removes the transition metal matrix in an area immediately adjacent to the working surface. The invention is claimed to increase the thermal resistance of the PCD material in the region where the matrix has been removed without compromising the strength of the sintered diamond.

US 6,544,308 and 6,562,462 describe the manufacture and behaviour of cutters that are said to have improved wear resistance without loss of impact strength. The PCD cutting element is characterised *inter alia* by a region adjacent the

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cutting surface which is substantially free of catalysing material. This partial removal (up to 70% of the diamond table being free of catalysing material) is said to be beneficial in terms of thermal stability.

Prior methods of removing the metal infiltrant from the PCD table typically require the use of extremely acidic mixtures (ph <1) at high temperature, for example, using hot hydrofluoric/nitric acid or hydrochloric/nitric acid mixtures. In addition prior art relating to the use of electrolytic means for infiltrant removal have decreasing effectiveness due to mechanisms such as the evolution of oxygen in the PCD matrix, which results in a slowdown of the reaction rate over time. This increases the resistance of the circuit and may eventually result in the suspension of the transition metal removal process.

SUMMARY OF THE INVENTION

According to the invention there is provided a method of treating a diamond containing body having at least one metal dispersed through its microstructure, the at least one metal being in the form of an anodic metal having a standard reduction potential $E_{\text{red}}^{\ominus}$ (anodic), the method including the step of treating the diamond containing body in order to remove some or all of the at least one metal from the diamond containing body, which treating step includes contacting the diamond containing body with a solution containing metal cations having a standard reduction potential $E_{\text{red}}^{\ominus}$ (cathodic), the metal cations being selected such that $E_{\text{red}}^{\ominus}$ (cathodic) - $E_{\text{red}}^{\ominus}$ (anodic) is greater than zero.

It is envisaged that the method of the invention can be applied to any diamond containing body that comprises one or more metals dispersed through its microstructure, wherein some or all of the one or more metals are advantageously removed from the diamond body.

The invention has particular application to treating a polycrystalline diamond (PCD) body, which has a second phase comprising a catalyst/solvent material

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located within interstices of the PCD microstructure, in order to remove some or all of the catalyst/solvent material from the PCD body.

The treating step preferably comprises contacting a surface or region of the diamond containing body to be treated with the metal cation solution.

The thickness of the diamond containing body may be in the region of about 100µm to about 5.0mm.

In a preferred embodiment of the invention, the diamond containing body is in the form of a PCD table that forms part of a PCD abrasive compact and defines a working surface, the method comprising contacting the working surface, or a region adjacent the working surface, of the PCD table with the metal cation solution in order to remove the catalyst/solvent from the region adjacent the working surface to a desired depth.

The diamond containing body may, for example, be contacted with the metal cation solution by immersing it, or a portion thereof to be treated, in the metal cation solution or by contacting it with an absorbent material, such as filter media or the like, soaked in the metal cation solution. Also it may be arranged in jigs or partially coated with a protective agent to avoid contact between the metal cation solution and sections of the diamond containing body which need to be protected from the treatment process. In the case of a PCD compact, these sections may be either the cemented carbide support or regions of the PCD compact itself.

In a particularly preferred embodiment of the invention, the metal cation is a copper cation, preferably provided by a copper sulphate solution at a concentration of about 1 g/l to about 316 g/l, in particular about 100 g/l.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will now be described in more detail, by way of example only, with reference to the accompanying figures in which:

Figure 1 shows an SEM micrograph of a cross-section through a PCD body treated in accordance with a preferred embodiment of a method of the invention; and

Figure 2 shows an SEM micrograph of a cross-section through a PCD body treated in accordance with another preferred embodiment of a method of the invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

This invention concerns a method of treating, in particular a method of leaching, a diamond containing body, such as a polycrystalline diamond (PCD) body or non-intergrown diamond containing body, for example.

As the method of the invention has particular application to the treatment of PCD bodies, for convenience, in what follows reference is made to leaching a PCD body containing a catalyst/solvent material. It is to be understood, however, that the invention extends to any diamond containing body that comprises one or more metals, where it is desirable to remove the one or more metals from the diamond containing body and which metals are capable of being leached from the diamond containing body by an appropriate metal cation containing solution.

Accordingly, in accordance with a preferred embodiment of the method of the invention, a sintered PCD compact having diamond to diamond bonding and having a second phase comprising a transition metal such as cobalt dispersed through its microstructure is provided. The PCD compact is typically formed in the presence of conventional diamond catalyst/solvent according to standard methods using HpHT conditions to produce a sintered PCD compact. The PCD compacts to be leached by the method of the invention typically have a thickness of about 100µm to about 5.0 mm.

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Typically, the PCD body is supported on, for example, a tungsten carbide support base to form a PCD compact or tool insert. The method may also apply to a PCD layer or part of a layer, free from or attached to a substrate of any type. It may be used to remove residual metal in the interface between the PCD grains, from regions or layers of the PCD surface or from the entire body.

In order to remove transition metal in the PCD compact, the PCD compact, in particular the working surface thereof, is contacted with a suitable metal cation solution under suitable conditions of concentration, temperature, pH, agitation and the like for a time sufficient to remove all or some of the transition metal to a desired depth, which may be the entire depth of the PCD body or a partial depth thereof.

The method relies on the driving voltage of the galvanic interaction determined by the choice of cathode, copper in the case of copper sulphate, and the transition metal, usually cobalt, present in the microstructure of the PCD compact. The copper, in this example, is more electronegative (tending to attract electrons to form a chemical bond) than the cobalt, and this voltage / reduction potential difference drives an electron transfer resulting in the depositing of copper out of the solution (it is seen on the PCD surface) and diffusion of the cobalt from the PCD table into the bulk solution.

Reduction or redox potential $E_{red}^{\ominus}$ (Volts) is the tendency of a chemical element / species to accept or attract electrons and ultimately be reduced. In reality, the electrons will bind to the element with which the standard reduction potential is higher.

The individual half reaction potentials of the electrochemical cell when summed according to the following equation yield $E_{cell}^{\ominus}$.

$$E_{cell}^{\ominus} = E_{red}^{\ominus}(\text{cathodic}) - E_{red}^{\ominus}(\text{anodic})$$

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In the case where $E_{\text{cell}}^{\ominus}$ is positive the reaction will be a spontaneous process termed a galvanic cell. Where $E_{\text{cell}}^{\ominus}$ is less than zero the reaction will be non-spontaneous and will need to be driven forward by an applied potential.

For the method of the invention to succeed, the selection of the cation metal must be such that its reduction potential when combined with that of the anodic metal yields a positive $E_{\text{cell}}^{\ominus}$.

The magnitude of the positive $E_{\text{cell}}^{\ominus}$ will be the electromotive driving force (Volts) behind the spontaneous reaction. The higher this driving force the faster the reaction will proceed.

The transition metal for anodic removal from a PCD compact is typically nickel, cobalt, or iron based, or an alloy thereof, typically cobalt. The standard reduction potentials for these 3 species, for example, at 25°C and 1 atm are detailed below:



Although copper sulphate has been used in exemplary embodiments of the invention as the source of metal cation for removing a transition metal, in particular Co, from a PCD material, any appropriate metal cation can be used, provided the $E_{\text{cell}}^{\ominus} > 0$ resulting in a galvanic interaction occurring. Cation solutions formed with the following, non-limiting, elements would also be considered suitable for this process: gold, silver, tungsten, mercury, platinum, rhenium, iridium, palladium, rhodium and ruthenium.

The standard reduction potential for two of the exemplary cations, Cu and Pd, are as follows:



The method sometimes includes the step of removing cation metal deposited on any portion of the PCD compact brought into contact with the metal cation solution.

The selection of the cation material is a fundamental part of the process. The use of palladium chloride rather than copper sulphate, for example, will reduce the process time, all other parameters kept constant. The choice of the metal cation will generally involve a trade off between the increased reaction rate and the cost of the reagents. As the intrinsic value of the cation increases the financial requirement to recover the cation will grow; due to the relatively low cost of copper it may be seen as a sacrificial cation. This may not be true for palladium or gold cations.

Modification of the metal cation concentration may affect the overall treatment time required to remove the anodic metal to the desired depth. As illustration of this an increase in the concentration of metal cation, in this example copper sulphate, from 100g/l to 300g/l results in a reduction in process time of 30% on average.

The nature of any electrochemical process is such that the operating temperature will play a role in the operating reaction rate. It has been determined that increasing the temperature to approximately 70°C from ambient temperature (approximately 15°C) can reduce the process time by over 50%. This relationship between the rate of reaction and the temperature is expected to continue as the temperature rises, and therefore the operation under pressure will allow further rate increases.

Regular and thorough agitation and diffusion of reacting elements to and from the boundary layer will improve the process reaction rate, in addition this regular agitation will also reduce the thickness of the boundary layer.

Another aspect of the impact of the above parameters is in terms of the solubility of the anodic metal in the cation solution. The cation solution will need to be

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considered in terms of pH, temperature and the other parameters to ensure that the anodic metal does not precipitate or similar in the bulk solution. This may be achieved by the addition of various complexers or the like. The precise additives used will depend on the anodic and cathodic metals and are well known to those familiar in the art.

In order to remove the anodic metal from the PCD table to the desired depth, it is important to keep the PCD table in contact with the metal cation for a sufficient period of time for this to be achieved. One way of doing so is to immerse the PCD table, or a portion thereof to be leached, in the metal cation solution. Where the PCD table is backed, for instance with a tungsten carbide support, the tungsten carbide support may need to be masked. Methods of masking PCD compacts prior to leaching are well known in the art, and include using an appropriate tape, masking liquid or the like. Once the desired leach depth has been achieved, the PCD table is washed and any deposited cation metal removed from the contact surface.

Using the method of the invention, it has been found that a backed PCD compact can be leached to a depth of in the order of 70 to 100 μm in a 24 hour treatment period. In addition to being able to carry out such 'shallow leaching' in a reasonable time period, it has been found that the method of the invention is capable of achieving leach depths in excess of 200 μm , and even as high as 250 μm . In practise there is no limit to the achievable leach depth, and the speed of anode metal removal can be increased as outlined already by the correct use of additional heat, agitation, ensuring solubility of removed metal, pH and complexants. It is envisaged that the method of the invention also provides for the possible leaching through the entire thickness of a PCD body, particularly at pressures above ambient pressure, resulting in a fully leached PCD body.

It has been found that a PCD compact can also be leached by placing the surface of the PCD adjacent the region to be leached on a membranous material, such as filter paper, for example, soaked in the metal cation solution. The advantage of this approach is that it is not necessary to mask the tungsten

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carbide support. Over a 24 hour leach period, leach depths of up to and exceeding 60 μm have been shown using this method.

The method has been shown to be favourably comparable to that of prior art treatment methods. Cost of reagents and ability to recycle these reagents is favourable compared to acidic leaching methods. The equipment and set up costs required to complete the leaching process using the method of the invention is very basic compared to the prior art, which often require specialised equipment capable of operating at high temperatures and pressures in the presence of dangerous reagents. In this regard, the reagents which may be used in the context of the present invention are considerably safer to handle for the user, which may even mean less skilful users may be used to carry out the treatment process. The process times for shallow leaching are comparable, under correct conditions, to those of the acidic leaching processes of the prior art; in addition, the deep leaching times are extremely favourable compared to the alternatives.

In addition to displaying a number of advantages over existing treatment methods, perhaps the most important contribution of the method of the invention over the prior art is the fact that the galvanic leaching process of the invention works so successfully, which in itself is somewhat surprising. It has previously been known that metals such as copper, silver, gold and platinum group metals can be recovered from acid solutions using a cementation process. In essence, this is a process in which copper or other valuable metals in solution are deposited on a particulate base metal higher up in the electromotive series. As cementation proceeds, the particulate base metal is coated with the valuable metal and the rate of cementation slows down, coming to a complete halt when the particulate base material is completely coated.

In the context of the present invention, such a tendency towards self-passivation would make it completely undesirable as an approach to removing a metal from a diamond containing body. It was therefore completely unexpected that in treating a diamond containing body in accordance with the method of the present invention that the metal cations did not precipitate on the removed metal, but

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rather precipitated on exposed surfaces of the diamond body. As a result, it is possible to treat a diamond containing body for a sufficient period of time to obtain desired and practical leach depths. The relative ease of removing the deposited metal from the diamond body once the desired leach depths have been reached is also advantageous.

The invention will now be illustrated, by way of example only, with reference to the following non limiting examples.

Example 1

Two hundred and eighty eight (288) standard tungsten carbide backed PCD compacts, having Co dispersed through their microstructure, were immersed in a 100g/l solution of copper sulphate for a period of 24 hrs. Prior to immersion, the tungsten carbide backings were masked by mechanical means to prevent contact with the copper sulphate solution. The treatment process was carried out at room temperature (approximately 15 to 25°C) and at a pH of 5.

At the end of the 24 hr treatment period, the treated PCD compacts were removed from the solution and washed in deionised water. Thereafter copper deposits on the treated PCD compacts were removed mechanically by brushing.

Samples of the treated PCD compacts were measured to determine leach depth and found to have an average leach depth of about 75.4 µm.

Example 2

One hundred (100) standard tungsten carbide backed PCD compacts, having Co dispersed through their microstructure, were placed on filter paper that had been soaked in a 100g/l solution of copper sulphate. The compacts were kept in contact with the CuSO₄ soaked filter paper for a period of 24 hrs, with regular replenishing of the CuSO₄ to ensure appropriate contact over the full treatment period. Unlike the PCD compacts of Example 1, there was no need for the

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tungsten carbide backings to be masked. The treatment process was once again carried out at room temperature (approximately 15 to 25°C) and at a pH of 5.

The treated PCD compacts were once again removed from the filter paper at the conclusion of the 24 hr treatment period and washed in deionised water. Thereafter copper deposits on the treated PCD compacts were removed mechanically by brushing.

Samples of the treated PCD compacts were measured to determine the depth of the leach and found to have an average leach depth of about 48 µm.

Example 3

Five (5) standard tungsten carbide backed PCD compacts, having Co dispersed through their microstructure, were immersed in a 100g/l solution of copper sulphate for a period of 24 hrs. Prior to immersion, the tungsten carbide backings were masked by mechanical means to prevent contact with the copper sulphate solution. The treatment process was carried out at approximately 70°C and at a pH of 5.

At the end of the 24 hr treatment period, the treated PCD compacts were removed from the solution and washed in deionised water. Thereafter copper deposits on the treated PCD compacts were removed mechanically by brushing.

Samples of the treated PCD compacts were measured to determine leach depth and found to have an average leach depth of 161 µm. The maximum leach depth achieved in this Example was as high as 242µm.

Example 4

Ten (10) standard tungsten carbide backed PCD compacts, having Co dispersed through their microstructure, were placed on filter paper that had been soaked in a weak Hydrochloric acid solution of 20g/l Palladium Chloride. The compacts were kept in contact with the PdCl₂ soaked filter paper for a period of 24 hrs, with

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regular replenishing of the PdCl_2 to ensure appropriate contact over the full treatment period. Unlike the PCD compacts of Example 1, there was no need for the tungsten carbide backings to be masked. The treatment process was once again carried out at room temperature (approximately 15 to 20°C) and at a pH of 3-4.

The treated PCD compacts were once again removed from the filter paper at the conclusion of the 24 hr treatment period and washed in deionised water. In this case no metal had deposited on the surface of the PCD compact.

Samples of the treated PCD compacts were measured to determine the depth of the leach and found to have an average leach depth of 37 μm .

CLAIMS

1. A method of treating a diamond containing body having at least one metal dispersed through its microstructure, the at least one metal being in the form of an anodic metal having a standard reduction potential $E^{\ominus}_{\text{red}}$ (anodic), the method including the step of treating the diamond containing body in order to remove some or all of the at least one metal from at least a portion of the diamond containing body, which treating step includes contacting at least a portion of the diamond containing body with a solution containing metal cations having a standard reduction potential $E^{\ominus}_{\text{red}}$ (cathodic), the metal cations being selected such that $E^{\ominus}_{\text{red}}$ (cathodic) - $E^{\ominus}_{\text{red}}$ (anodic) is greater than zero.
2. A method according to claim 1, wherein the metal cation is selected from the group consisting of copper, gold, silver, tungsten, mercury, platinum, rhenium, iridium, palladium, rhodium and ruthenium.
3. A method according to claim 1 or claim 2, wherein the at least one metal is a transition metal.
4. A method according to claim 3, wherein the at least one metal is selected from cobalt, nickel, iron, and alloys thereof.
5. A method according to any one of the preceding claims, wherein the at least one metal is cobalt and the metal cation is a copper cation.
6. A method according to claim 5, wherein the copper cation is provided by a copper sulphate solution.
7. A method according to any one of the preceding claims, wherein the diamond containing body is a polycrystalline diamond (PCD) body.

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8. A method according to claim 7, wherein the at least one metal is a diamond catalyst/solvent material contained in the interstices of the PCD microstructure.
9. A method according to any one of the preceding claims, wherein the diamond containing body forms part of a diamond abrasive compact and defines a working surface, the method comprising contacting the working surface, or a region adjacent the working surface, with the metal cation solution in order to remove some or all of the at least one metal from the region adjacent the working surface to a desired depth.
10. A method according to any one of the preceding claims, wherein the diamond containing body has a thickness of from about 100 μ m to about 5.0mm.

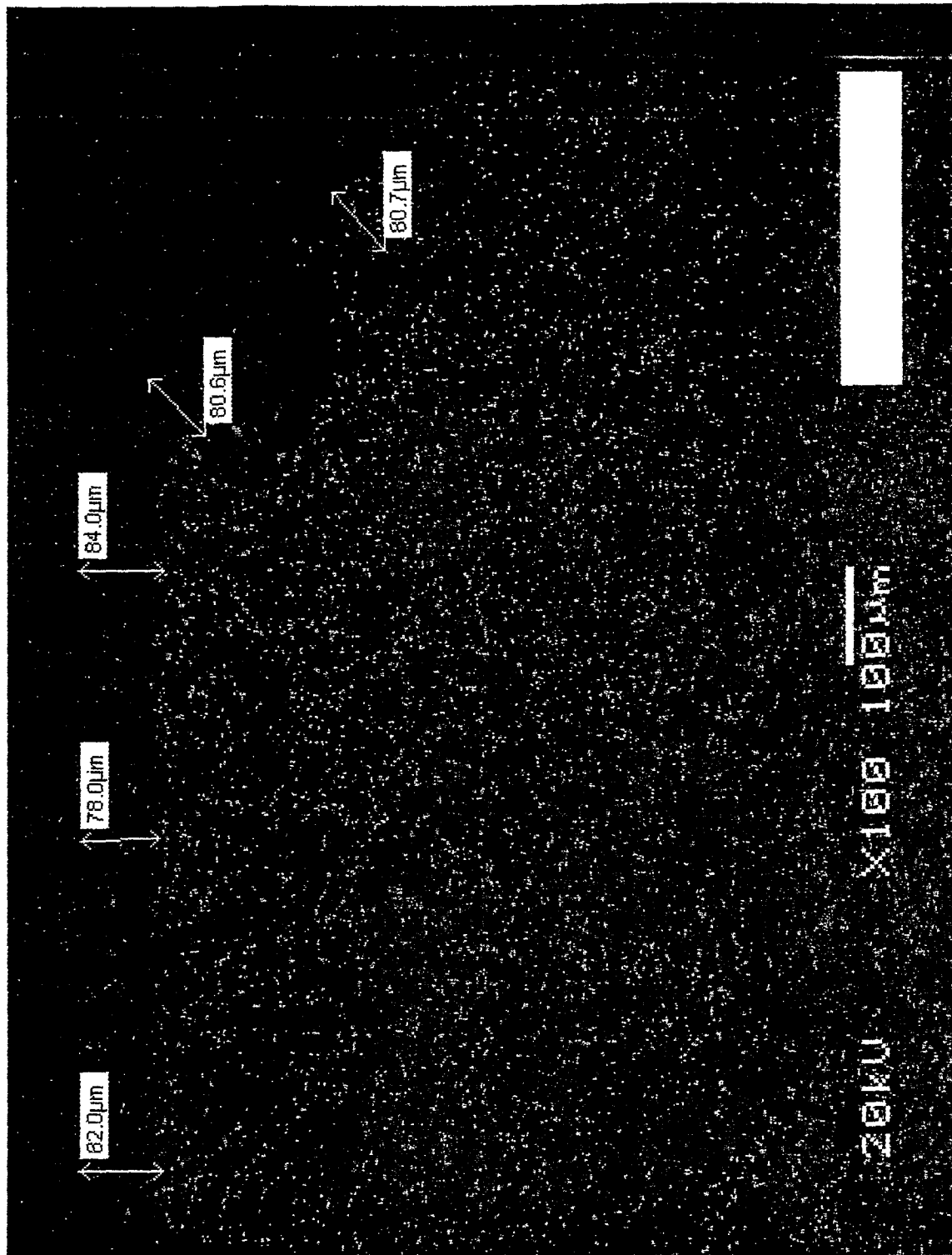


Fig. 1

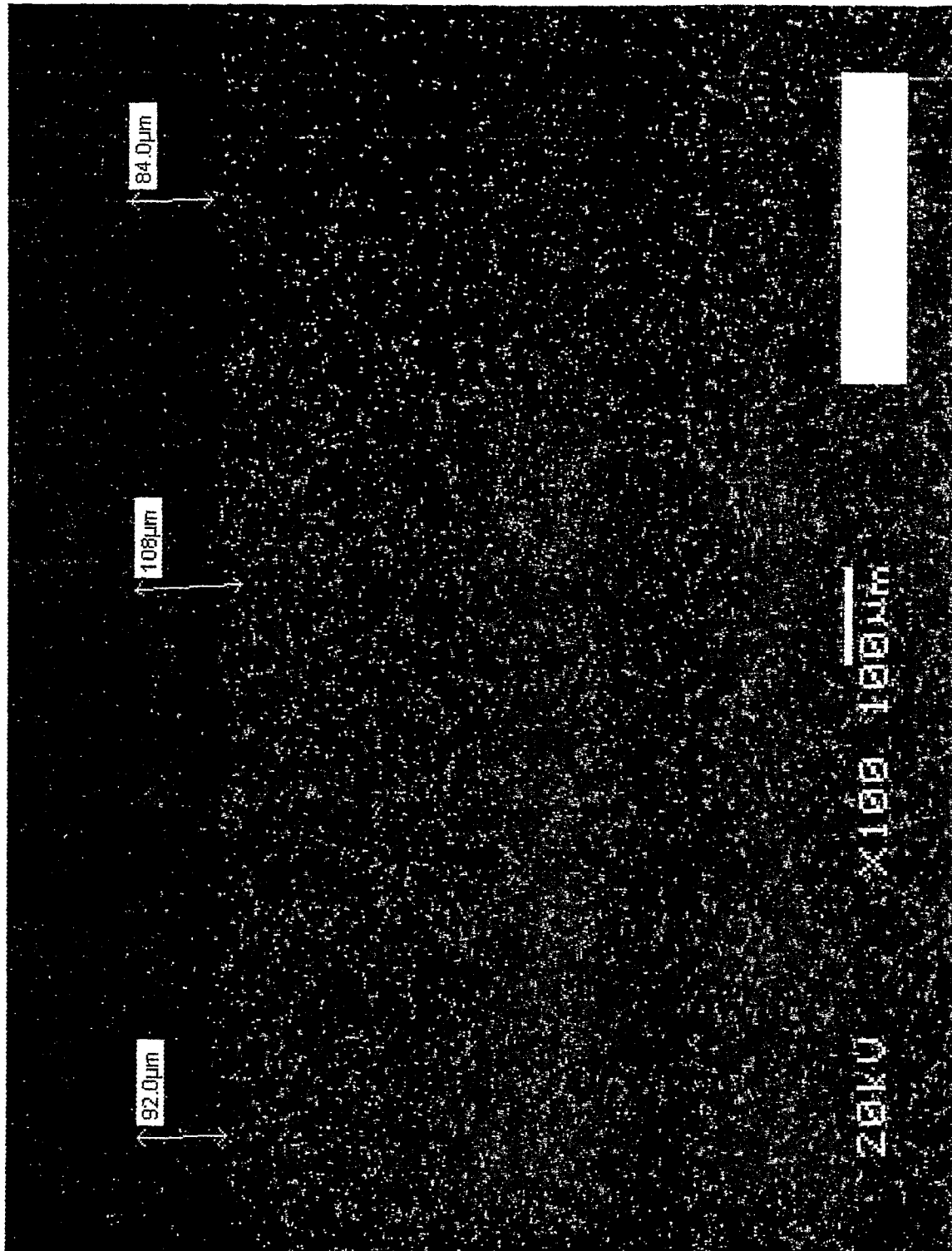


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2010/050211

A. CLASSIFICATION OF SUBJECT MATTER

INV. B22F3/24 C22C26/00 C25F5/00
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)

C22C C25F C04B B22F

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 practical, 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	US 6 562 462 B2 (GRIFFIN NIGEL DENNIS [GB] ET AL) 13 May 2003 (2003-05-13) column 5, line 52 - column 6, line 38 column 10, line 28 - line 39 column 12, line 16 - line 38 figures	1-10
X	GB 1 598 837 A (GEN ELECTRIC) 23 September 1981 (1981-09-23) page 2, line 28 - line 30 page 3, line 12 - line 55 claims 9,15	1-6,9,10
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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

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Date of the actual completion of the international search

15 June 2010

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Ceulemans, Judy

INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2010/050211

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2005/139397 A1 (ACHILLES ROY D [ZA] ET AL ACHILLES ROY DERRICK [ZA] ET AL) 30 June 2005 (2005-06-30) paragraph [0033] paragraph [0038] paragraph [0043] - paragraph [0047] -----	1-10
A	EP 1 195 810 A1 (SUMITOMO ELECTRIC INDUSTRIES [JP]) 10 April 2002 (2002-04-10) paragraph [0020]; examples -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2010/050211

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