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(54) Benævnelse: **Fremgangsmåde til fjernelse af en hårdmaterialecoating**

(56) Fremdragne publikationer:
WO-A1-99/64646
WO-A1-2015/139731
US-A- 3 083 165
US-A- 4 720 332
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A METHOD FOR REMOVING A HARD MATERIAL COATING

The present invention relates to a method for removing a hard material coating, which is applied onto the substrate of a tool. The invention further relates to a material mixture, an aqueous solution as well as an electrolyte for use in this method.

Background of the invention

Cutting tools, which are used in the field of metal processing, e.g., as milling tools, are exposed to high mechanical and thermal stress. In order to improve the cutting performance as well as prolong service live, these tools are coated with hard materials on the working surfaces following their mechanical production. These hard materials in general are compounds of refractory metals (elements of the 4^{th}, 5^{th} and 6^{th} secondary group of the periodic table, such as Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W) with the elements B, C, N, O and Si.

In spite of their hardness and wear resistance, however, these hard material coatings will be subject to wear in use such that at the end of service life the layer will not meet the requirements anymore. In order to continue being able to use the tool, which usually is undamaged, it has to be re-coated. For the successful application of a layer by means of vacuum technology (PVD or CVD) it is necessary that the surface to be coated is free of affecting contaminations; these also including residues of a previous coating.

Classical methods for decoating a tool include the mechanical decoating by means of grit (such as, for example, grit blasting the tool) until the hard material coating has been removed. In the mechanical removal of a hard material coating, high forces exert upon the tool, which may lead to deformation and mechanical damage of the substrate.

As an alternative to mechanical decoating methods, there are further used chemical decoating methods, wherein the hard material coating is being dissolved. Due to the chemical resistance of such hard material coatings, however, there have to be used very aggressive chemicals, which in part will also dissolve the carrier material or uncoated parts, respectively, of the tool.

A known method for the chemical removal of AlTiN on hard metal substrates uses a mixture of concentrated sulphuric acid and potassium permanganate. This gives rise to the unstable and potentially explosive intermediate product, manganese heptoxide (Mn_2O_7), which acts as

the oxidation agent proper. This method, however, has proven to be inefficient, necessitating increased safety requirements such that it is not used in practice.

In WO 99/64646 A1 there is described a method, in which the hard material coating is attached to an intermediate layer applied to the substrate. By means of a solution, which may penetrate pores in the hard material coating, this intermediate layer is dissolved, which, as a consequence, also leads to the removal of the hard material coating. The solution comprises hydrogen peroxide, dinatrium oxalate and sodium hydroxide. Apart from the increased efforts necessary due to the application of the intermediate layer, this method, like the chemical method described above, has the disadvantage that the uncoated substrate is chemically attacked.

SHORT DESCRIPTION OF THE INVENTION

It is the task of the present invention to completely remove a hard material coating present on a tool, without damaging any uncoated substrate.

This task is solved by a method for removing a hard material coating from the substrate of a tool, comprising the provision of an electrolyte, which comprises an aqueous solution with 4 to 6 mol/l OH^-, 0.1 to 0.5 mol/l S^{2-} and 0.5 to 2 mol/l of oxalate, placing the tool in the electrolyte and dissolving the hard material coating by contacting the tool with a direct current voltage source. This electro-chemical method for dissolving the hard material coating has proven to be advantageous, as the substrate material in such an electro-chemical method will form a water-insoluble sulphide, which serves as a passivation, whereby the underlying substrate is protected. At the same time, the hard material coating is dissolved. This effect is advantageous in particular in uncoated areas of the substrate or in such areas, which no longer have any coating.

Basically, it is sufficient if the substrate has at least one of the metals W, Co or Fe or any other metal, which can form sulphides that are water-insoluble. Preferred substrate materials, hence, comprise W, Co and/or Fe, as these form passivating sulphide layers.

In some tools having a hard material coating, there may be introduced a basis layer between hard material coating and substrate. For example, in an AlTiN hard material coating, there is frequently provided a TiN basis layer. This basis layer may simply be removed following the removal of the hard material coating in a next step. For this purpose, there may preferably be provided that the tool is treated with a mixture comprising NH_3 and H_2O_2 after removing the

hard material coating in order to remove a basis layer arranged between the hard material coating and the substrate. The mixture comprises preferably a freshly prepared solution from an aqueous NH_3 solution and an aqueous H_2O_2 solution.

In one embodiment variant there is provided that the basis layer is TiN.

The method according to the invention may be used for any hard material coating if the hard material coating contains at least one of the above mentioned refractory metals (Ti, Zr, Hf, V, Nb, Ta, Cr, Mo or W). The best results have been achieved in first tests with hard material coating made from AlCrN or AlTiN.

It has further proven to be advantageous if the tool is galvanically provided with a metal layer, for example, a cobalt layer, on those parts of the substrate having no hard material coating.

For the electro-chemical method there has been proven as advantageous a material mixture, consisting of

- 70 to 87 mol% of a metal hydroxide,
- 1 to 6 mol% of a water-soluble sulphide,
- 11 to 24 mol% of an oxalic acid or a salt of the oxalic acid
- at the most 2 mol% of miscellaneous ingredients,

which is why this constitutes one aspect of the invention.

From the material mixture itself or also by means of the individual ingredients, there may be provided an aqueous solution such that also an aqueous solution for a method for removing a hard material coating from the substrate of a tool, comprising

- 4 to 6 mol/l of OH^-
- 0.1 to 0.5 mol/l of S^{2-}
- 0.5 to 2 mol/l of oxalate,

constitutes one aspect of the invention.

The aqueous solution is preferably characterized by

- 4.8 to 5.2 mol/l of OH^-, preferably KOH or NaOH
- 0.24 to 0.27 6 mol/l of S^{2-}, preferably K_2S or Na_2S
- 0.8 to 1.2 mol/l of oxalate, preferably disodium oxalate or dipotassium oxalate.

The aqueous solution comprises preferably further ingredients in a total amount of not more than 2 mol/l. Especially preferably, the aqueous solution does not comprise any further ingredients.

A further aspect relates to an electrolyte with such an aqueous solution for a method for removing a hard material coating from the substrate of a tool.

Further details and advantages are explained in the following by way of examples and figures.

There is shown:

Fig. 1: SEM picture of a hard metal substrate (5000x)

Fig. 2: EDX spectrum of the hard metal substrate of fig. 1

Fig. 3: SEM picture of a high-speed steel substrate (5000x)

Fig. 4: EDX spectrum of the high-speed steel substrate of fig. 3

Fig. 5: SEM picture of a TiN/AlTiN layer (1000x)

Fig. 6: EDX spectrum of the TiN/AlTiN layer of fig. 5

Fig. 7: SEM picture of an AlCrN layer (1000x)

Fig. 8: EDX spectrum of the AlCrN layer of fig. 7

Fig. 9: Photographs of contacted and lacquered samples

Fig. 10: Association of the SEM pictures with the respective zones of the samples according to fig. 9

Fig. 11: System hard metal – TiN/AlTiN: initially uncoated hard metal substrate after electro-chemical treatment, 1000x

Fig. 12: System hard metal – TiN/AlTiN: hard metal electro-chemically decoated of TiN/AlTiN

Fig. 13: System hard metal – TiN/AlTiN: transition from initially uncoated hard metal substrate (left) to untreated hard metal (right).

Fig. 14: System hard metal – TiN/AlTiN: transition from initially uncoated hard metal substrate (top) to decoated hard metal (bottom)

Fig. 15: System hard metal –AlCrN: initially uncoated hard metal substrate following electro-chemical treatment, 1000x

Fig. 16: System hard metal –AlCrN: hard metal electro-chemically decoated of AlCrN

Fig. 17: System hard metal –AlCrN: transition from initially uncoated hard metal substrate (left) to untreated hard metal (right).

Fig. 18: System hard metal –AlCrN: transition from initially uncoated hard metal substrate (top) to decoated hard metal (bottom)

Fig. 19: System high-speed steel – TiN/AlTiN: initially uncoated high-speed steel substrate following electro-chemical treatment, 1000x

Fig. 20: System high-speed steel – TiN/AlTiN: high-speed steel electro-chemically decoated of TiN/AlTiN

Fig. 21: System high-speed steel – TiN/AlTiN: transition from initially uncoated high-speed steel substrate (left) to untreated high-speed steel (right).

Fig. 22: System high-speed steel – TiN/AlTiN: transition from initially uncoated high-speed steel substrate (top) to decoated high-speed steel (bottom).

Fig. 23: System high-speed steel – AlCrN: initially uncoated high-speed steel substrate following electro-chemical treatment, 1000x

Fig. 24: System high-speed steel – AlCrN: high-speed steel electro-chemically decoated of AlCrN

Fig. 25: System high-speed steel – AlCrN: transition from initially uncoated high-speed steel substrate (left) to untreated high-speed steel (right).

Fig. 26: System high-speed steel – AlCrN: transition from initially uncoated high-speed steel substrate (top) to decoated high-speed steel (bottom).

Fig. 27: Co-layer on hard metal following decoating process

Fig. 28: Hard metal decoated of TiN/AlTiN following coating of the exposed hard metal with cobalt

DETAILED DESCRIPTION OF THE INVENTION

The examined samples (according to the substrate) were composed of high-speed steel as well as hard metal. The samples were coated with TiN/AlTiN or AlCrN, respectively. The hard metal coating was incomplete as it was important for the determination whether the task posed had been completely solved that uncoated parts were present on the substrate and in order to show that these are not being affected by the electro-chemical coating.

The task was solved by the development of an alkaline electrolyte, which contains oxalate and sulphide ions. The sulphide ions form together with the substrate an insoluble phase, which protects via passivation against an attack by the decoating process.

Another possibility to protect areas, which had been uncoated from the beginning on, was to selectively apply onto these a thin layer in a galvanic way. In the case described, this was a Co layer.

Experimental mode:

At the beginning of the decoating attempts, the initial state of the samples was recorded by means of SEM:

The round blanks that had been provided were wrapped with wire for contacting, and all faces except for the half front faces were covered with coating lacquer. In this way, there is given in the following examinations, e.g., in the scanning electron microscope, the direct comparability with the initial status (fig. 9).

Decoating attempts in detail
Electro-chemical decoating using alkaline electrolyte
In order to protect the substrate, in particular the co-phase of the hard metal, during the decoating process, there were tested sulphide containing electrolytes. For this reason, sulphide is an ideal candidate as all substrate materials (W, Co, Fe) will form water-insoluble sulphides in the alkaline, which protect the material against further attack by passivation, whereas the elements in the PVD layer (Al, Ti, Cr) do not form such phases and, hence, remain electro-chemically active.

Using a solution (5M KOH + 20g/l Na_2S + 1M $K_2C_2O_4$) there was decoated as follows:
Hard material coating AlCrN: 60°C, 200 mV vs. Hg/HgO, 25 min
Hard material coating TiN/AlTiN: 60°C, 600 mV vs. Hg/HgO, 45 min

This electrolyte has proven to be the best among the candidates tested, giving good results in all four sample types in regard to the decoating performance and the area removal.

The fig. 11 to 26 are depictions of four representative locations of four decoated samples having different substrate/layer combination, i.e. the fig. 11 to 14, 15 to 18, 19 to 22 and 23 to 26 respectively represent one sample. The first of the respectively associated figures (this is fig. 11, 15, 19 or 23, respectively) represents the initially uncoated substrate following the electro-chemical treatment, with the respectively second fig. (this is fig. 12, 16, 20 or 24, respectively), representing the decoated substrate. The respectively third fig. (this is fig. 13, 17, 21 or 25, respectively) represents the transition from the treated, initially uncoated substrate to the originally uncoated substrate protected by lacquer during the treatment, thus serving to represent the substrate change during the treatment. The respectively fourth fig. (this is fig. 14, 18, 22 or 26, respectively) represents the transition from the decoated substrate to the treated, but initially uncoated substrate.

The decoating of hard metal / TiN/AlTiN worked well. Fig. 20 shows the exposed hard metal substrate following the decoating, with an attack being recognizable, which is, however, significantly weaker than with the systems tested so far. At the decoated locations, the substrate is only attacked at those locations, where there are present pores in the TiN / AlTiN layer (fig. 21). At the transitions (fig. 22 and 23), there is to be seen that the attack has only small effects on the dimensions of the substrate.

The basis layer made from TiN of the TiN/AlTiN coating may be removed using a mixture of NH_3 (25%) and H_2O_2 (30%) in a proportion of 1+3 at room temperature within 4-5 minutes, without affecting the substrates. This mixture should always only be freshly prepared in small amounts (<50ml), as H_2O_2 will rapidly disintegrate in an alkaline condition. Dissolved heavy metals (Co, Fe) will catalyse the disintegration, leading to a strong heating and formation of foam. Alternatively, the solution may be applied onto the substrates by means of a spraying method, wherein the solution is prepared only immediately upstream of the atomiser nozzle using a static mixer.

Also with this system decoating will be possible, without strongly affecting the substrate. As the decoating process with AlCrN will be realized more gently than with TiN/AlTiN, the substrate attack will be lower.

The electrolyte system will also work with high-speed steel substrates, as expected. Decoating is complete, the attack on the substrate being only a minimum.

Also AlCrN may be removed from high-speed steel substrates using this system. Also here there is to be seen that the attack on the substrate is lower than with the system high-speed steel – TiN/AlTiN due to the milder conditions when removing AlCr.

Galvanic co-layer as additional substrate protection:
By a selective, thin galvanic coating of the hard metal substrate, the attack on the substrate was further restricted. In the precise case, there was selected cobalt, as it constitutes the matrix material of the hard metal and its use, hence, does not introduce any undesired contaminations into the system.

In principle, as a protection there is suitable any galvanically separable metal or any alloy, which is insoluble in the decoating electrolyte and which may subsequently be removed, without attacking the substrate (e.g., iron, zinc, manganese, copper, etc.). When coating, it has been surprisingly shown that the TiN/AlTiN layer may be coated in spite of its lower

electric conductivity and the ceramic structure at high current values with cobalt in an adhering way. The attempt to nevertheless decoat this sample (based on the consideration that the adherence cobalt layer on the TiN/AlTiN coating is not as good as on the hard metal) failed, as the cobalt layer has proven to be firmly adhering and insoluble, which in principle confirmed the original concept stating that a cobalt layer will protect the underlying material. In the subsequent removal of the cobalt layer, the exposed substrate material was naturally attacked heavily. The coating with cobalt with significantly reduced current density left the TiN/AlTiN layer more or less free such that the subsequent decoating could be performed without any problems at the free locations (see fig. 27 and 28).

The method of reducing the current density in the galvanic coating constitutes a fast and simple solution, which uses the lower electric conductivity of the coating in comparison to the substrate in order to prevent a galvanic coating of the free substrate.

Patentkrav

1. Fremgangsmåde til fjernelse af en hårdmaterialecoating fra substratet af et værktøj, omfattende

• tilvejebringelse af en elektrolyt, som omfatter en vandig opløsning med 4 til 6 mol/l OH^-, 0,1 til 0,5 mol/l S^{2-} og 0,5 til 2 mol/l oxalat,

• placering af værktøjet i elektrolytten og

• opløsning af hårdmaterialecoatingen, ved at værktøjet bringes i kontakt med en jævnspændingskilde.

2. Fremgangsmåde ifølge krav 1, **kendetegnet ved, at** værktøjet efterfølgende behandles med en blanding, omfattende NH_3 og H_2O_2, for at fjerne et basislag, der er anbragt mellem hårdmaterialecoatingen og substratet.

3. Fremgangsmåde ifølge krav 1 eller krav 2, **kendetegnet ved, at** basislaget er TiN.

4. Fremgangsmåde ifølge et af kravene 1 til 3, **kendetegnet ved, at** hårdmaterialecoatingen består af AlCrN eller AlTiN.

5. Fremgangsmåde ifølge et af kravene 1 til 4, **kendetegnet ved, at** værktøjet inden placeringen i elektrolytten forsynes galvanisk med et metallag, fortrinsvis koboltlag, på de dele af substratet, som ingen hårdmaterialecoating har.

6. Materialeblanding til fremstilling af en vandig opløsning ifølge krav 7, bestående af

• 70 til 87 mol% af et metalhydroxid,

• 1 til 6 mol% af et vandopløseligt sulfid,

• 11 til 24 mol% oxalsyre eller et salt af oxalsyren

• maksimalt 2 mol% af øvrige bestanddele.

7. Vandig opløsning for en fremgangsmåde til fjernelse af en hårdmaterialecoating fra substratet af et værktøj ifølge krav 1, omfattende

- 4 til 6 mol/l OH^-
- 0,1 til 0,5 mol/l S^{2-}
- 0,5 til 2 mol/l oxalat.

8. Vandig opløsning ifølge krav 7, **kendetegnet ved**
- 4,8 til 5,2 mol/l OH^-, fortrinsvis KOH eller NaOH
- 0,24 til 0,27 6 mol/l S^{2-}, fortrinsvis K_2S eller Na_2S
- 0,8 til 1,2 mol/l oxalat, fortrinsvis dinatriumoxalat eller dikaliumoxalat.

9. Vandig opløsning ifølge krav 7 eller krav 8, **kendetegnet ved, at** den vandige opløsning omfatter øvrige bestanddele i en samlet mængde på ikke mere end 2 mol/l.

10. Vandig opløsning ifølge krav 7 eller krav 8, **kendetegnet ved, at** den vandige opløsning ingen yderligere bestanddele omfatter.

11. Elektrolyt for en fremgangsmåde til fjernelse af en hårdmaterialecoating fra substratet af et værktøj ifølge krav 1, omfattende en materialeblanding ifølge krav 6 eller en vandig opløsning ifølge et af kravene 7 til 10.

12. Galvanisk celle, omfattende en elektrolyt ifølge krav 11.

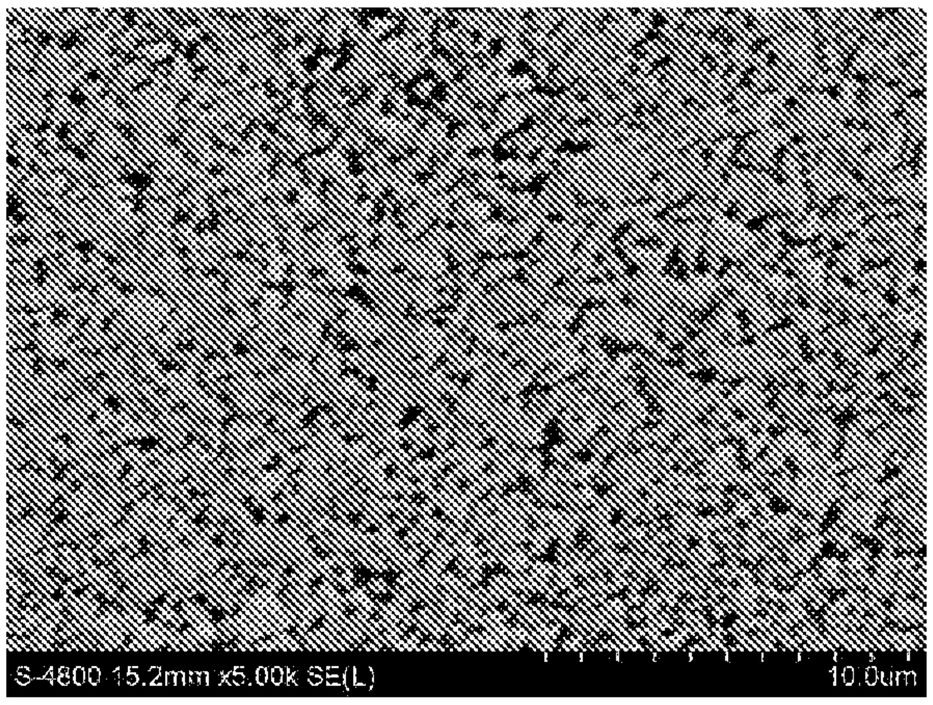

Fig. 1

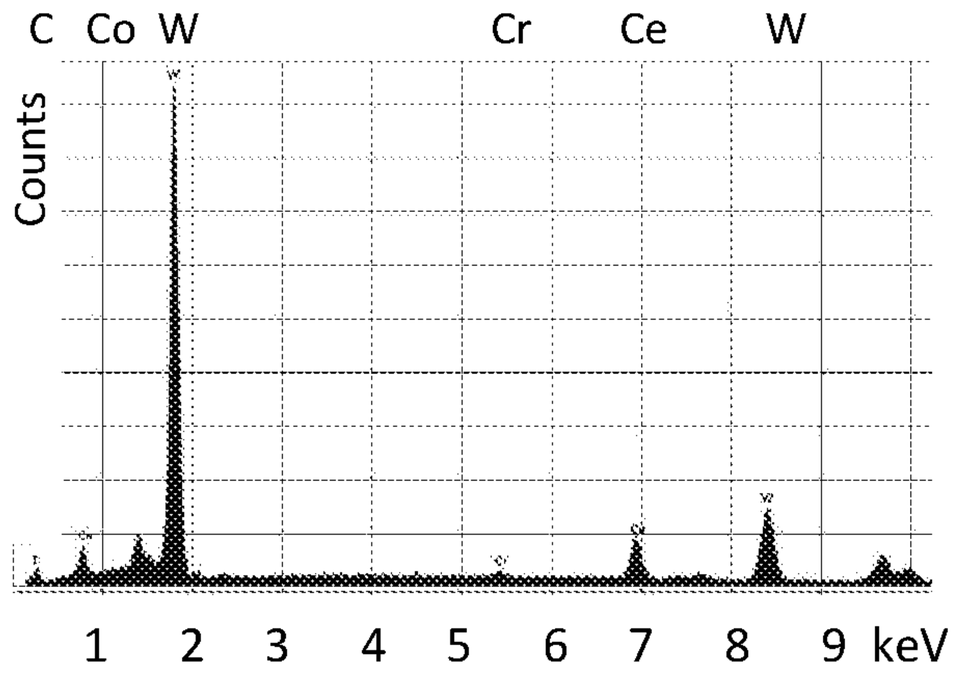

Fig. 2

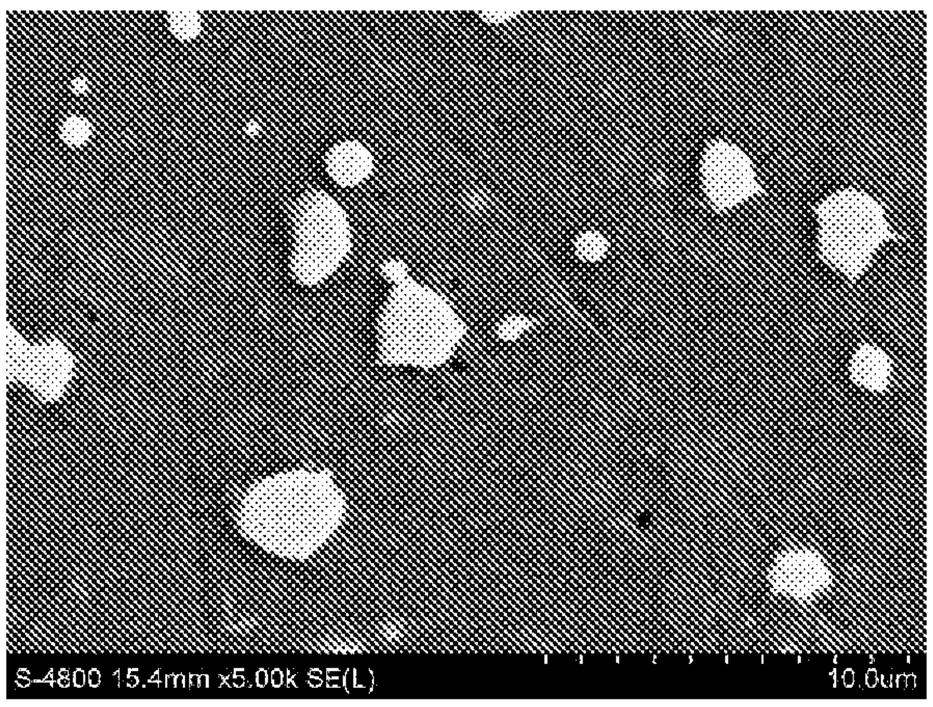

Fig. 3

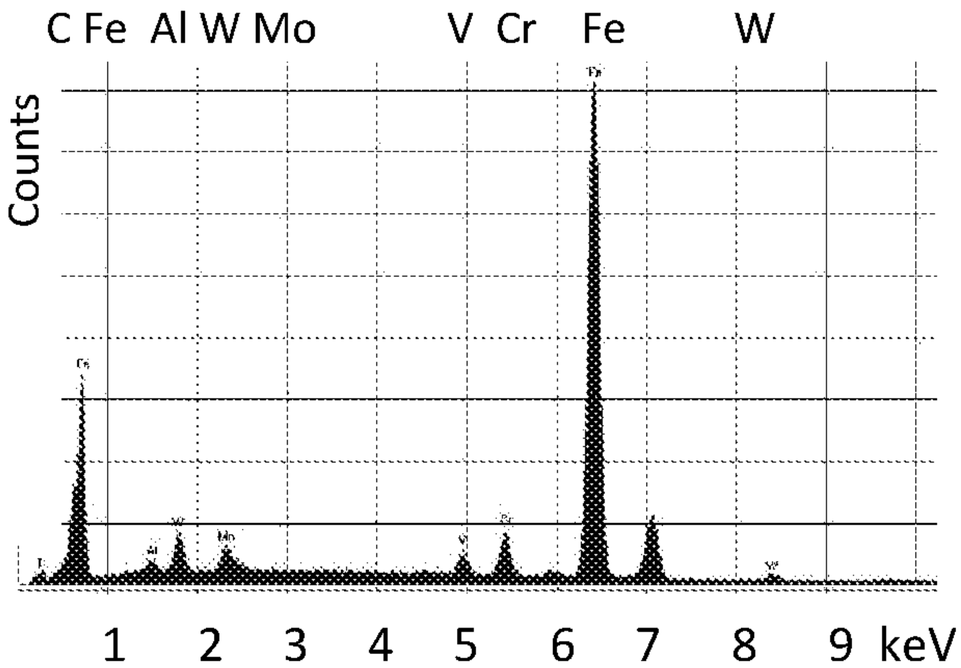

Fig. 4

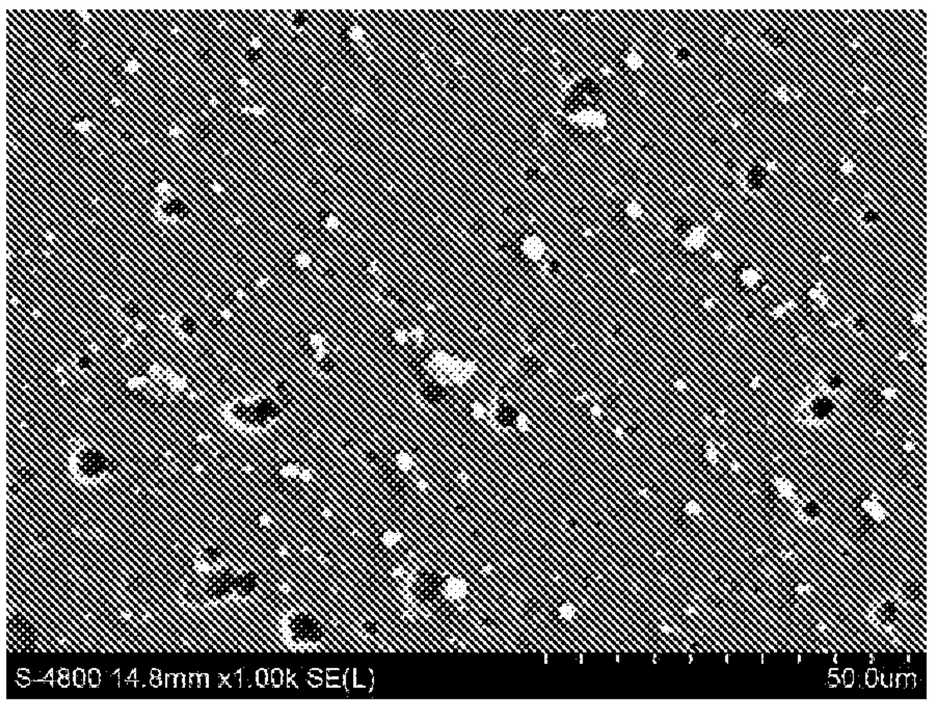

Fig. 5

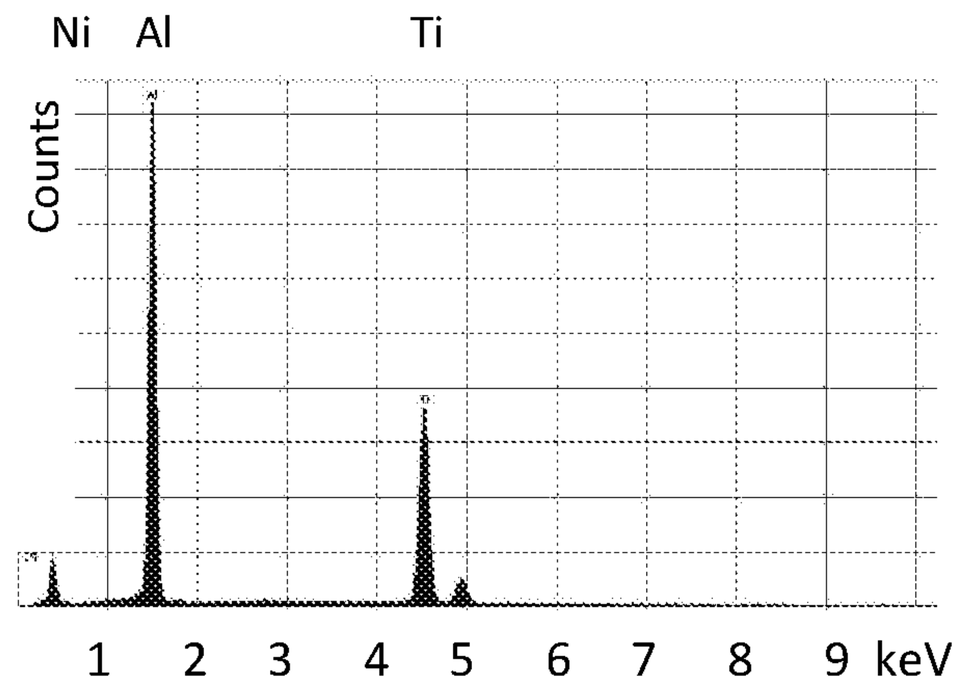

Fig. 6

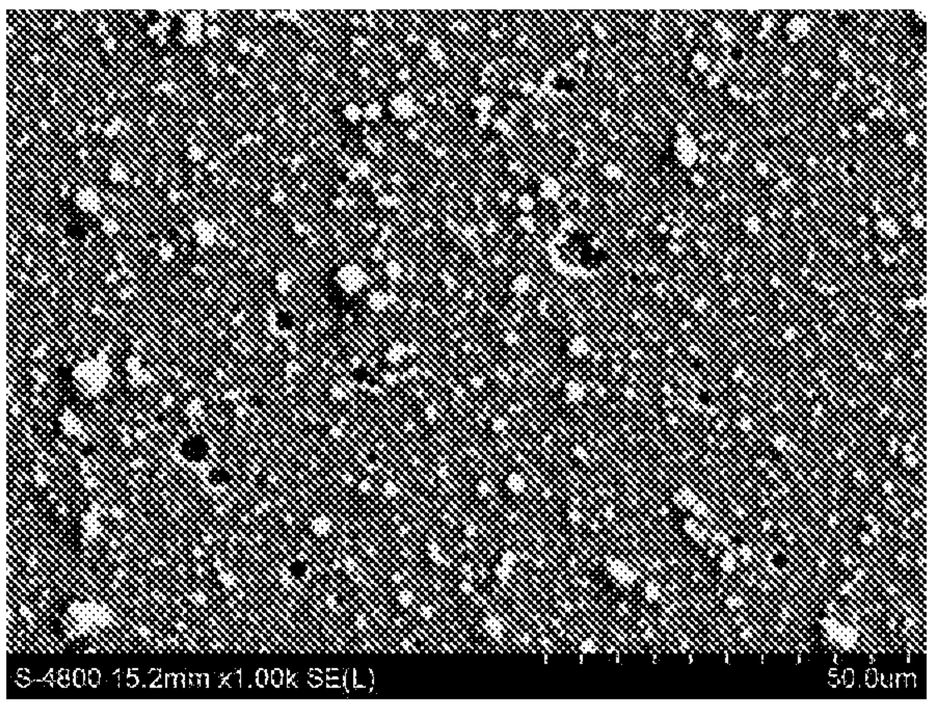

Fig. 7

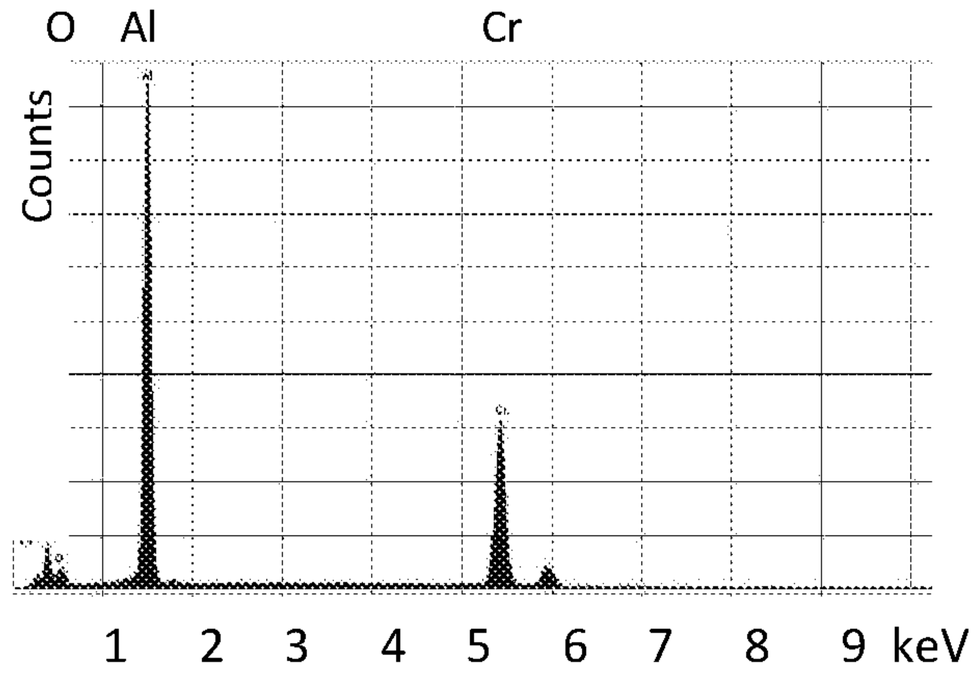

Fig. 8

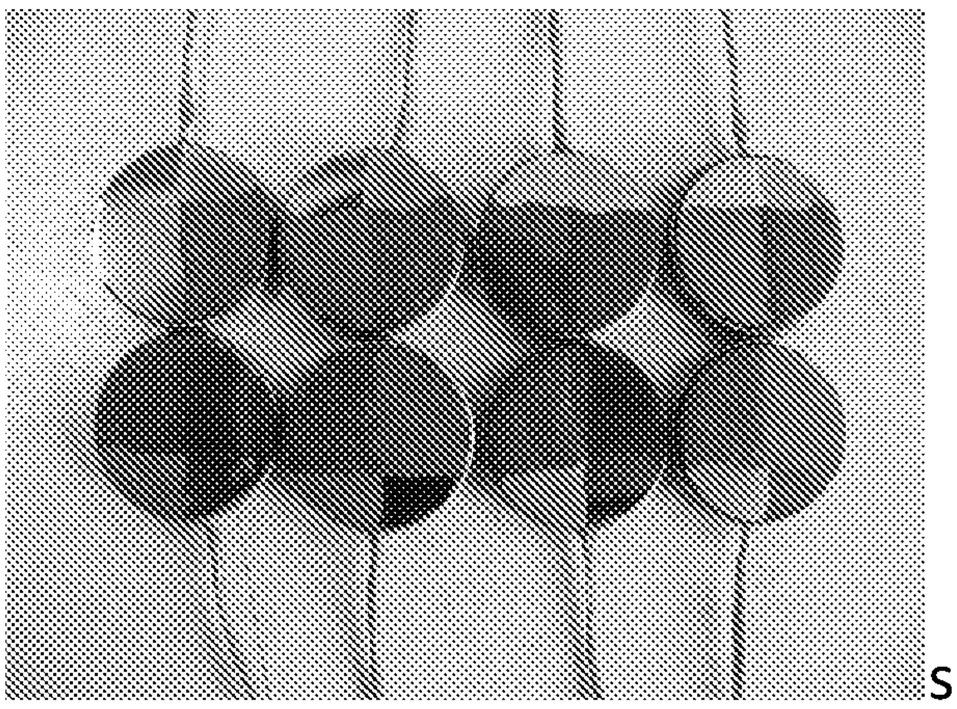

Fig. 9

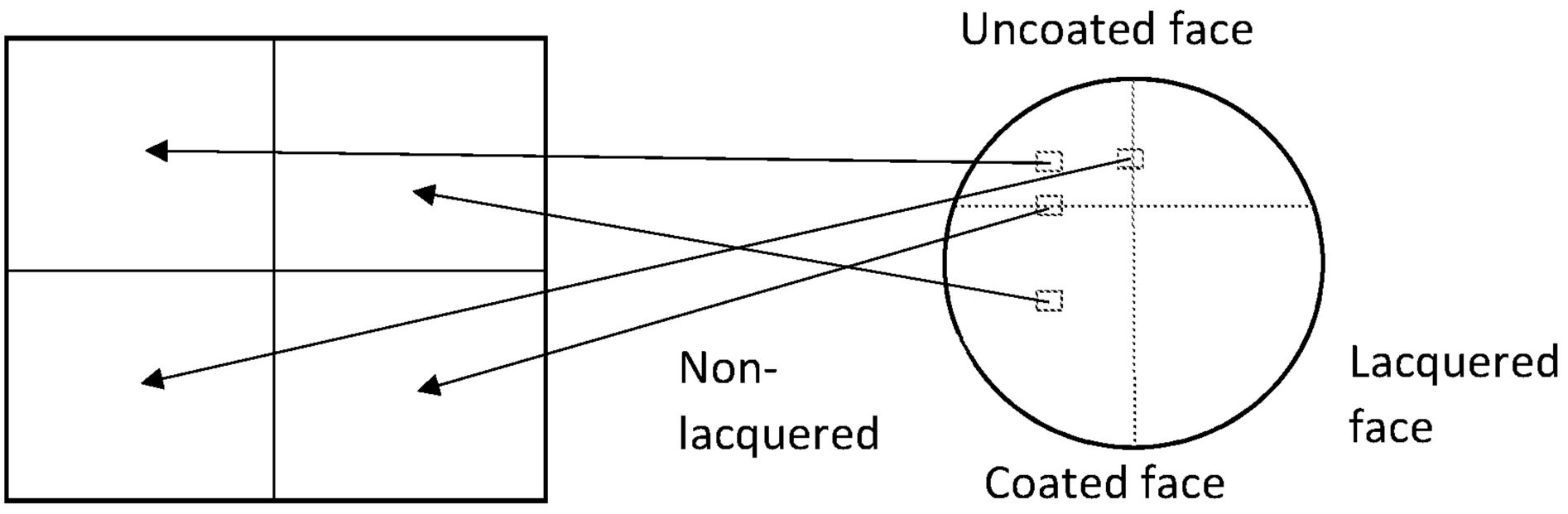

Fig. 10

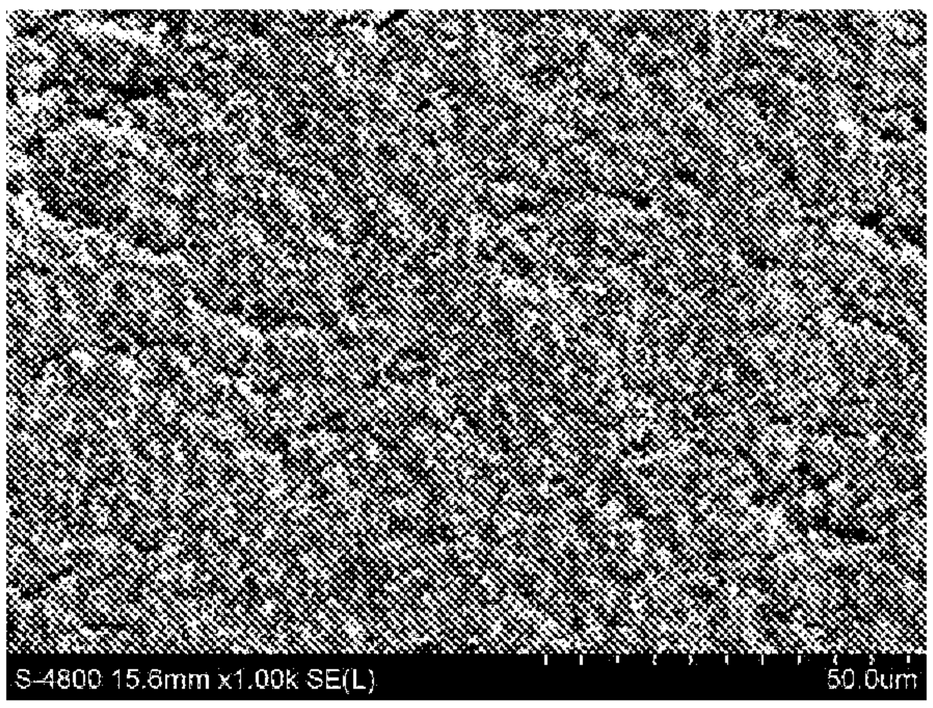

Fig. 11

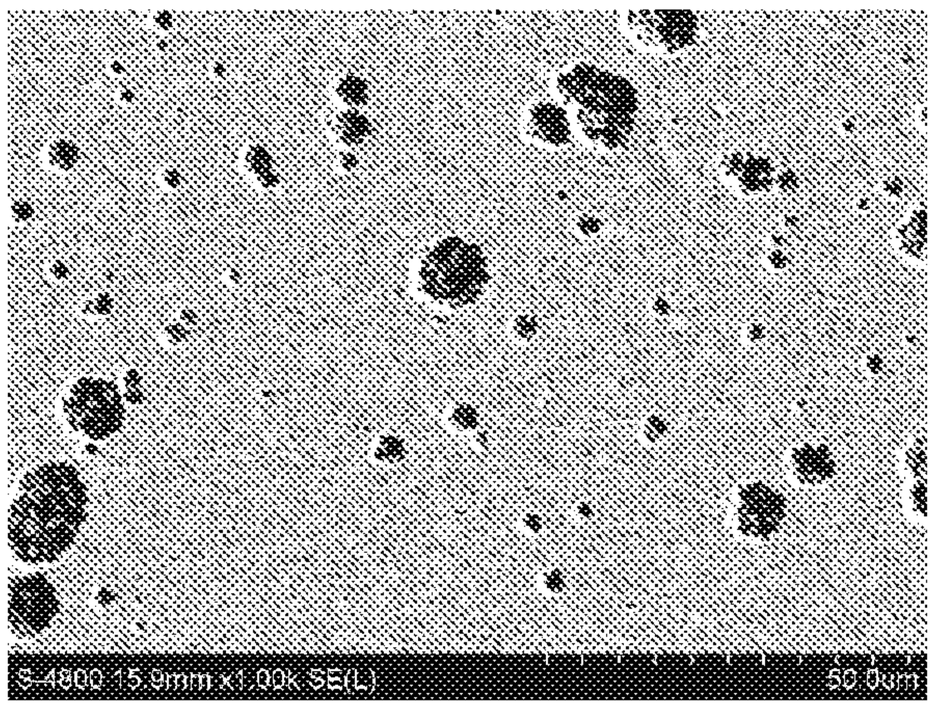

Fig. 12

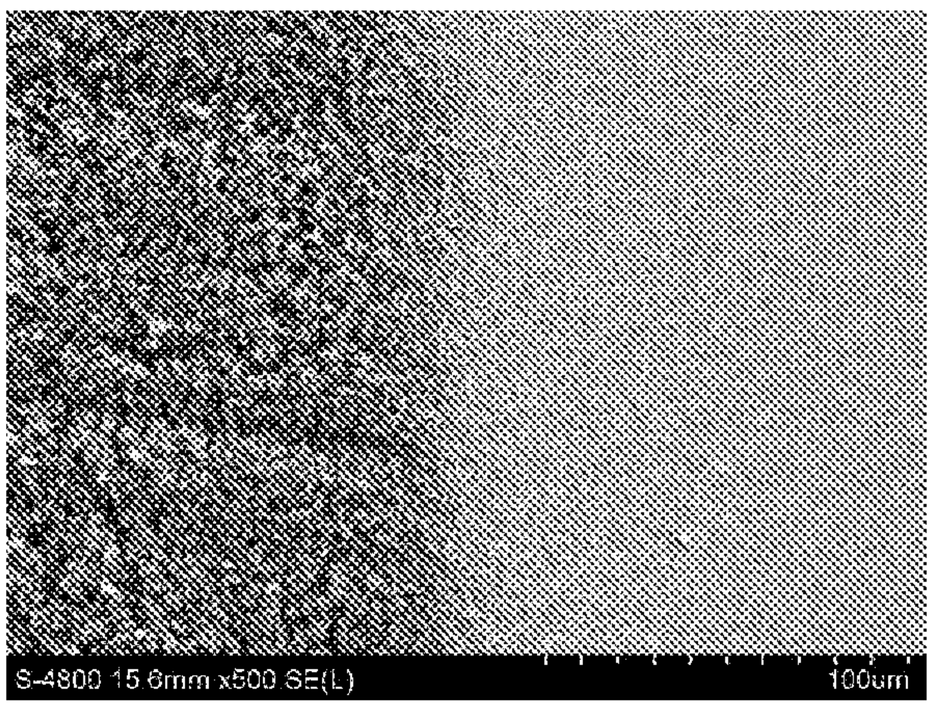

Fig. 13

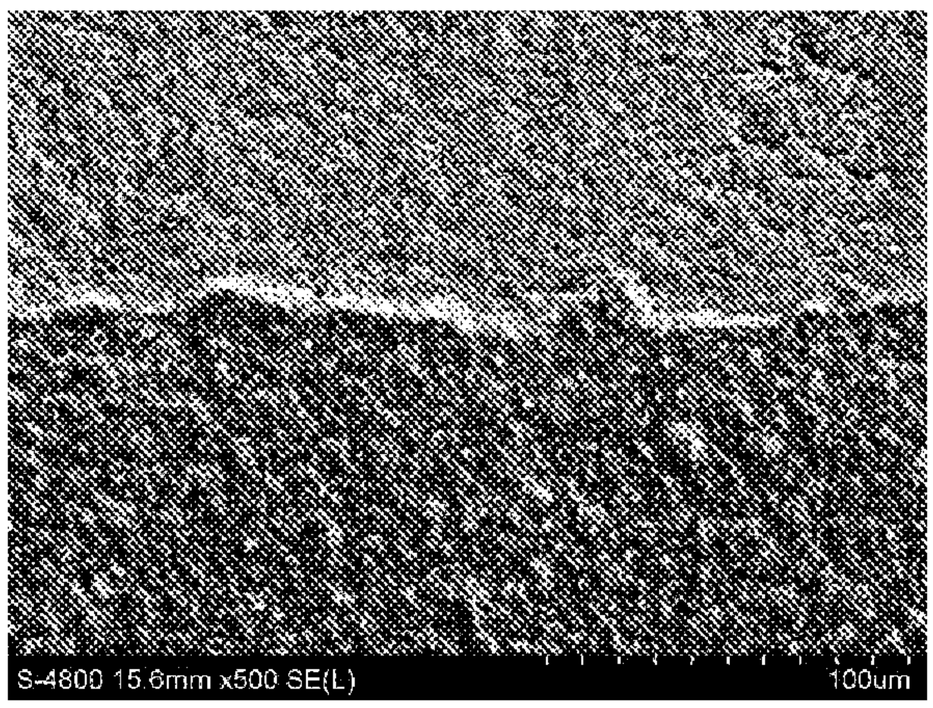

Fig. 14

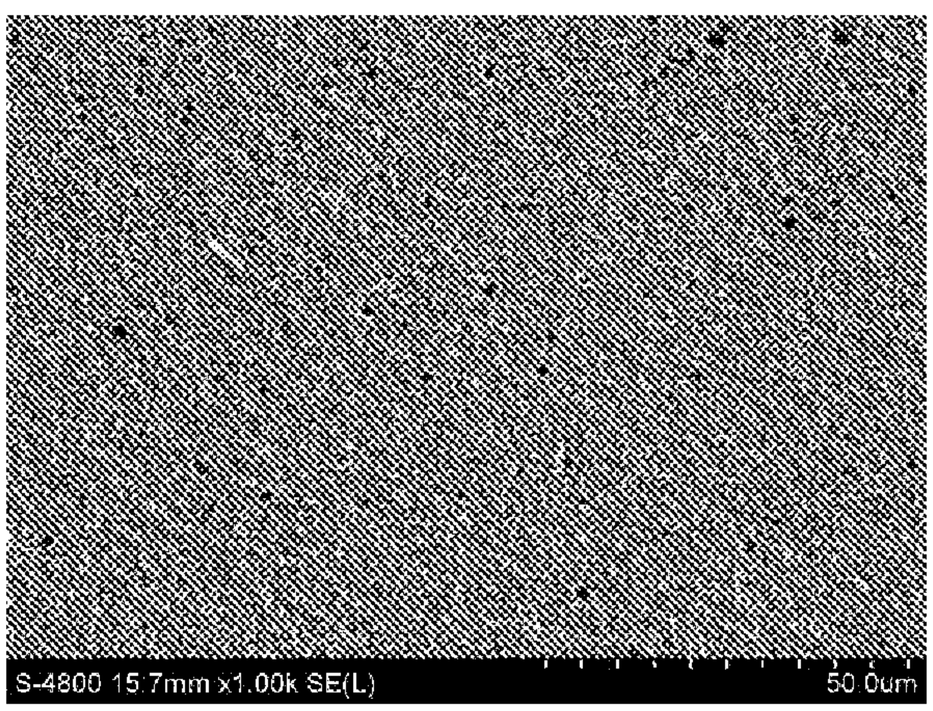

Fig. 15

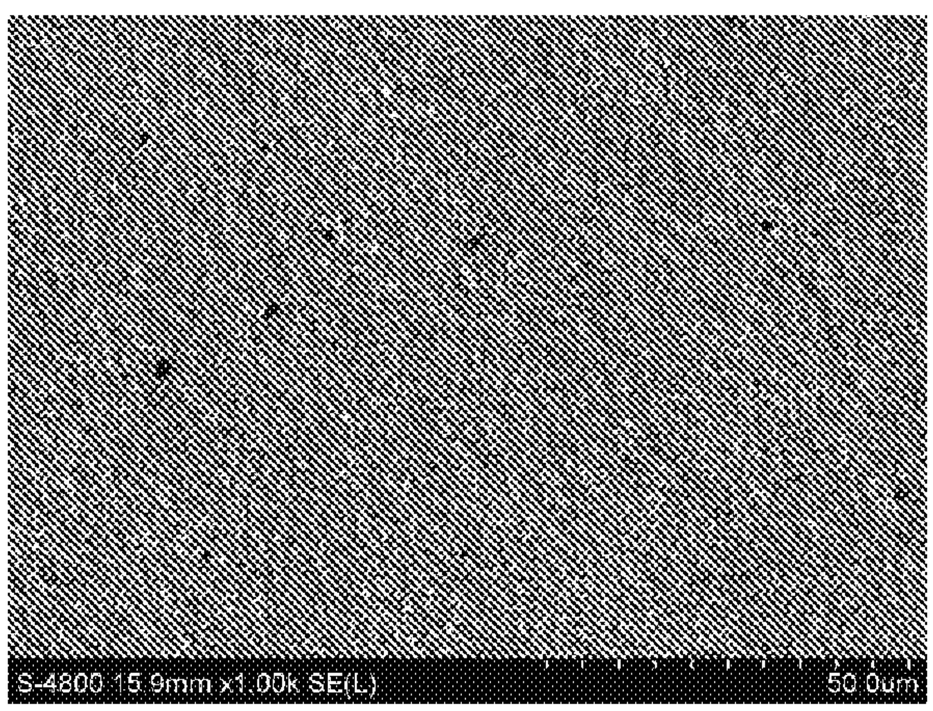

Fig. 16

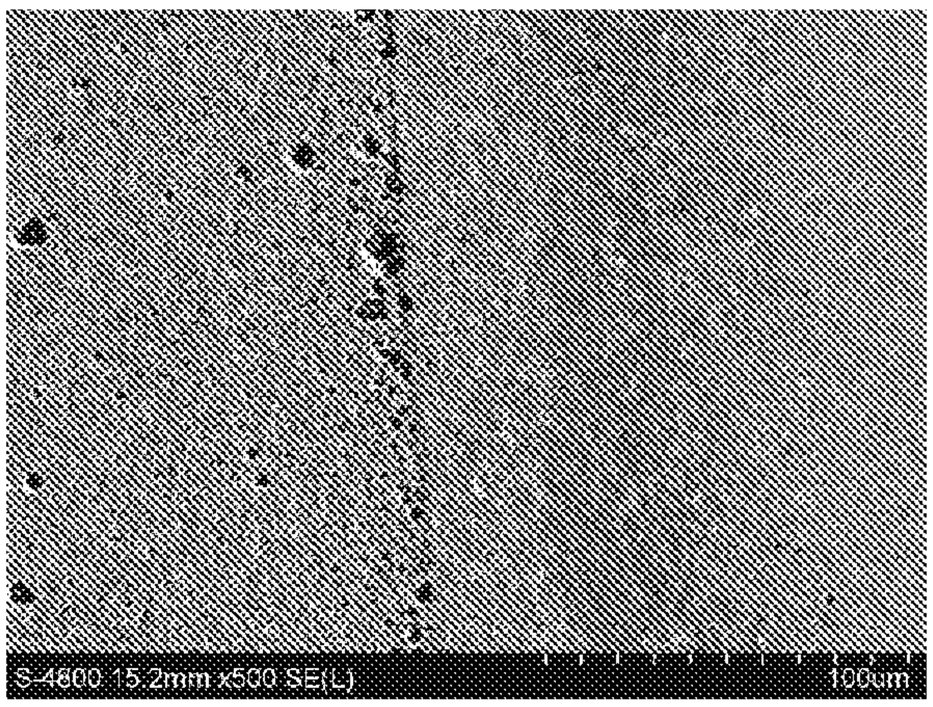

Fig. 17

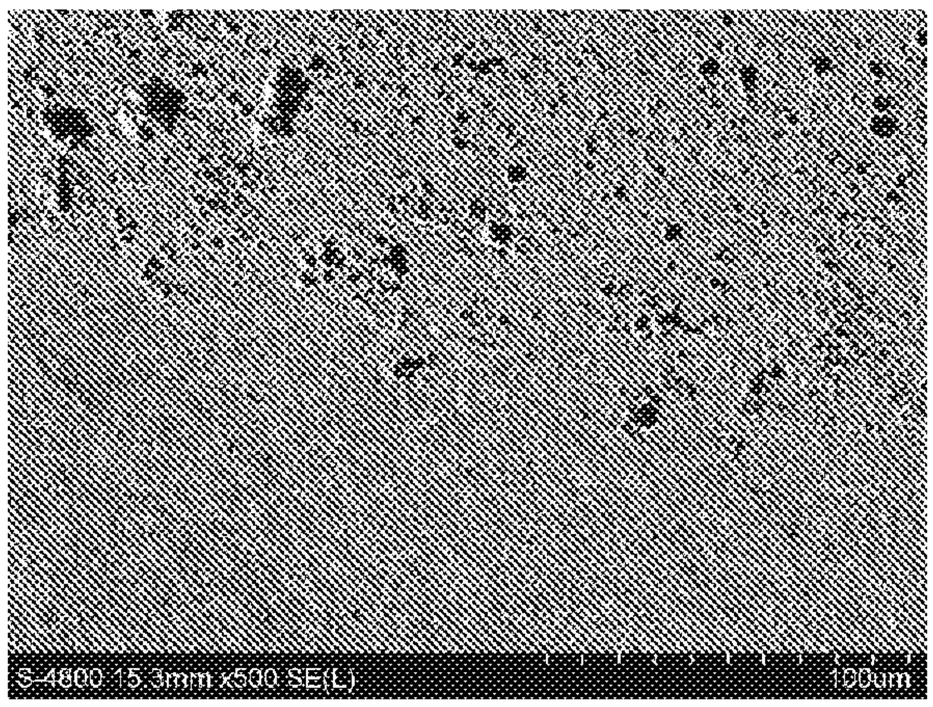

Fig. 18

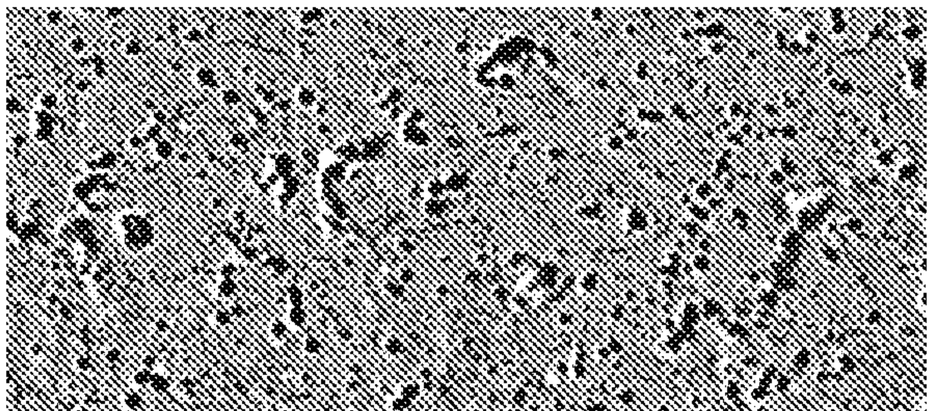

Fig. 19

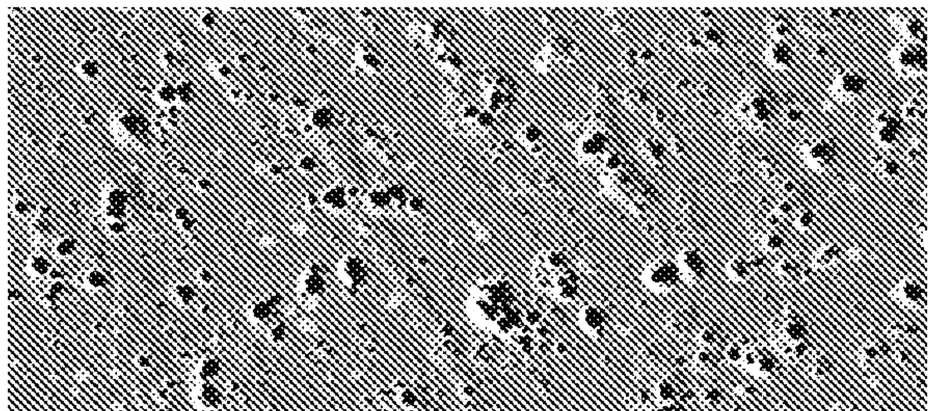

Fig. 20

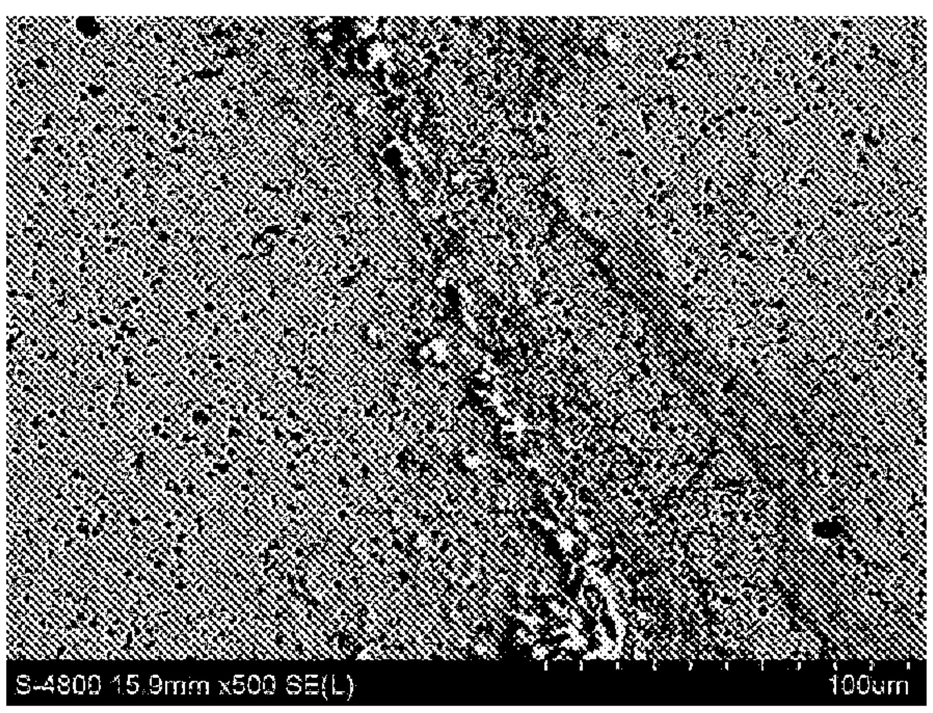

Fig. 21

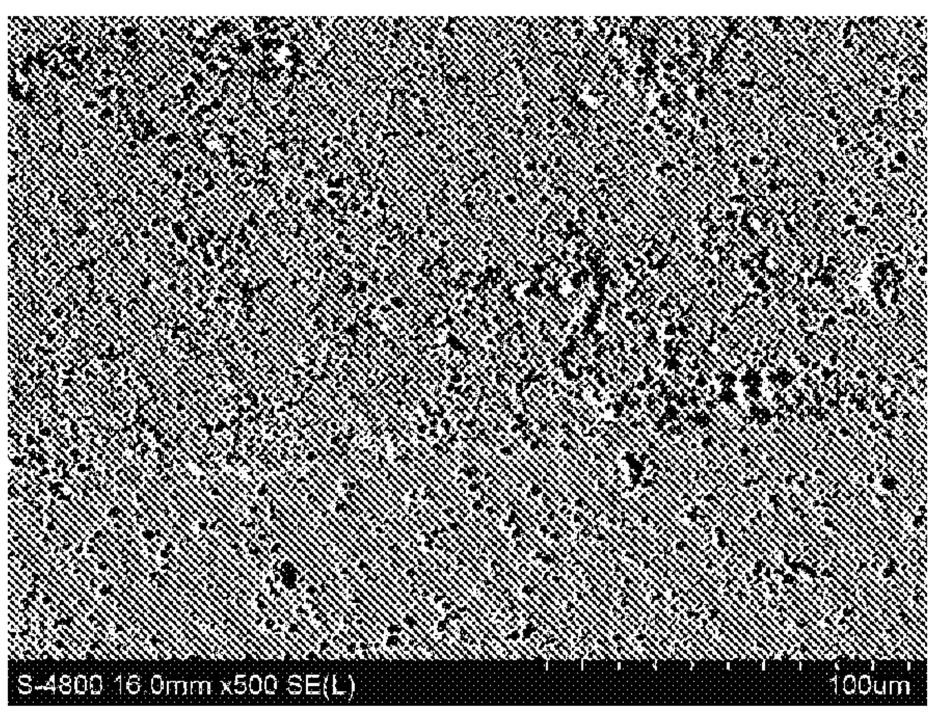

Fig. 22

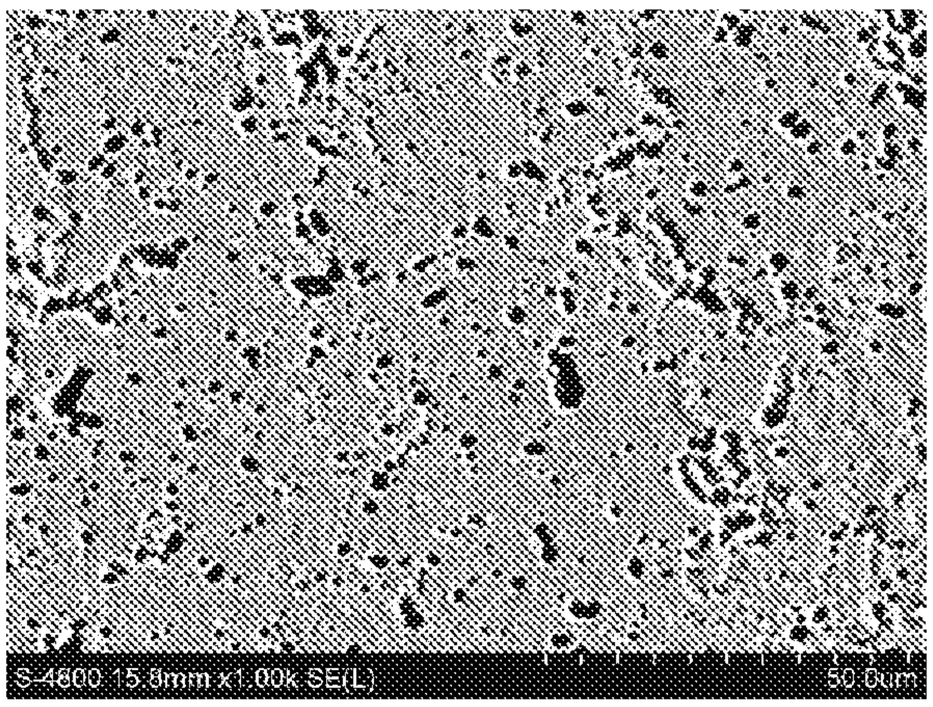

Fig. 23

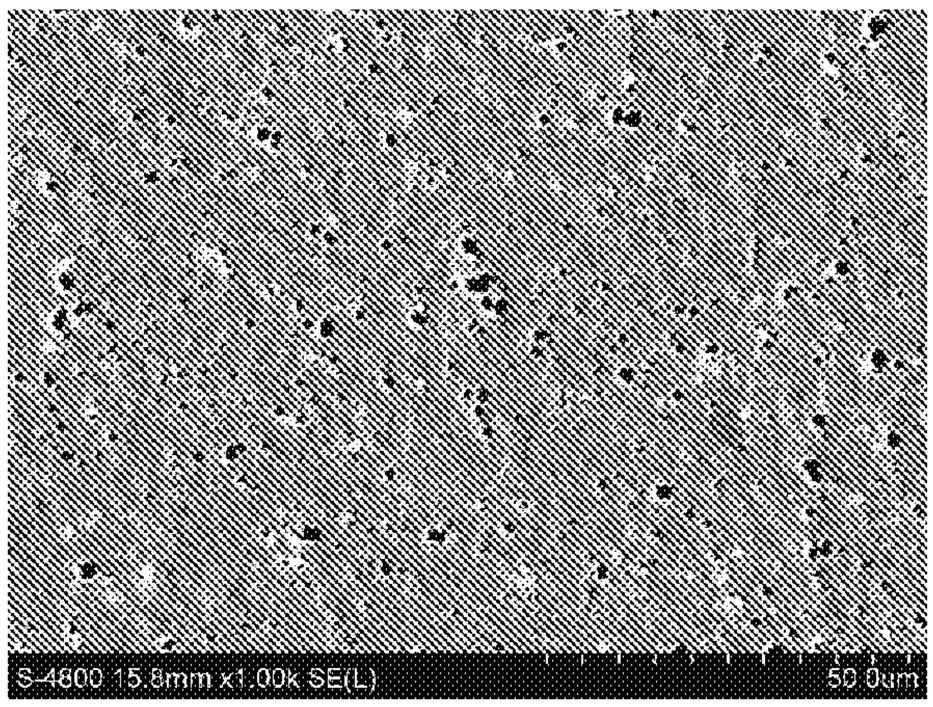

Fig. 24

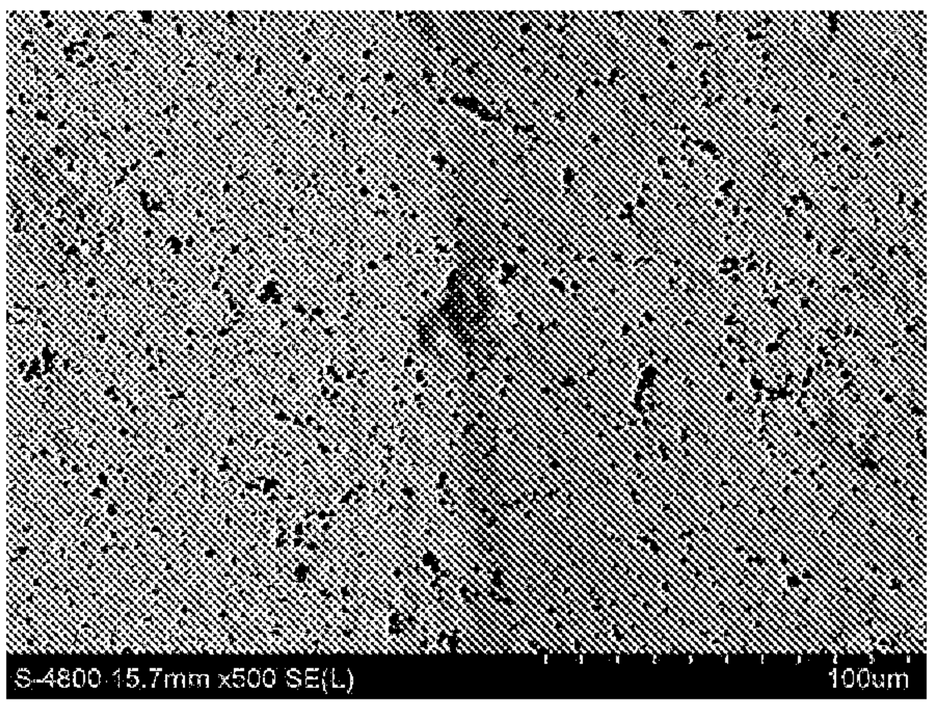

Fig. 25

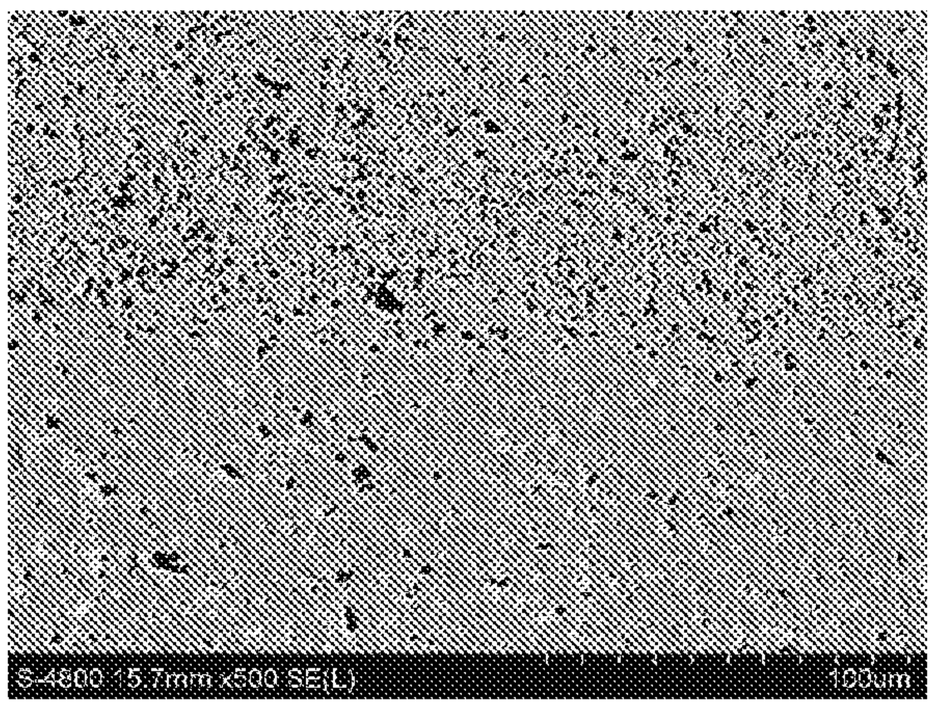

Fig. 26

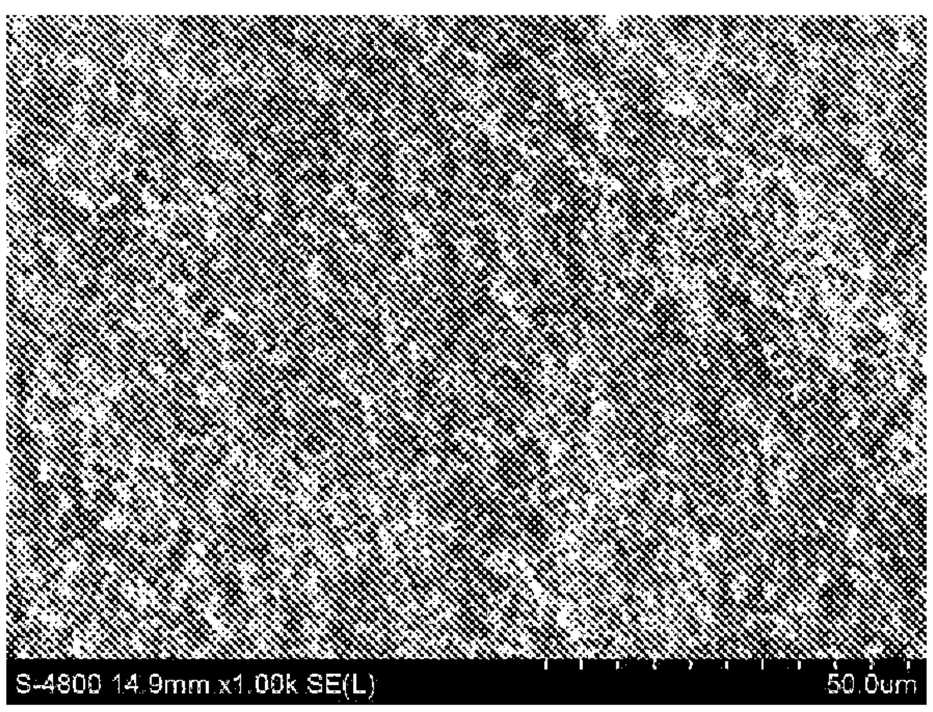

Fig. 27

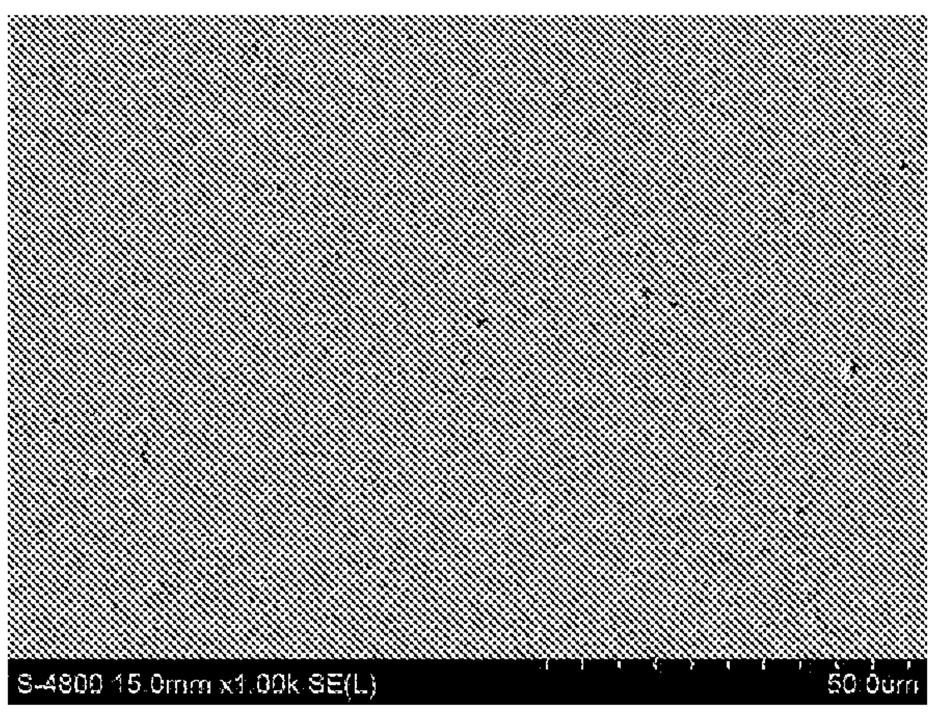

Fig. 28