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Description

The present invention relates to a process for obtaining a protective coating for metallic surfaces subjected to both thermal and mechanical wear, for example, subjected simultaneously to wear by sliding and friction and to oxidation, such as the surfaces of elements comprising the combustion chamber of a heat engine, for example, the cylinders, valve stems, piston crowns and, above all, piston rings. The invention further relates to a protective coating obtained by the process.

It is known that the components of modern heat engines, and in particular the elements of the combustion chamber of a diesel engine, are subjected to high thermal and mechanical stresses. In particular the sliding surfaces of the cylinders, pistons, valve stems and, above all, the piston rings, must have extremely high properties of resistance and thermal stability at high temperature, resistance to adhesive and abrasive wear and to seizure, to fatigue, to oxidation and to both chemical and electro-chemical corrosion, as well as to fretting. Such requirements have until now been at least partly satisfied by using for the said elements heavily alloyed cast iron covered with coatings of various types, both of the electro-plated type and the type obtained by flame or a coating obtained by plasma spray. Known electro-deposited coatings are principally obtained by means of coating a layer of chrome onto a base layer of nickel deposited on the surface to be protected. The thickness of the coating thus obtained does not exceed about 0.45 mm because layers of greater thickness would not be economic given the long deposition times required and, above all, because they would be incoherent, therefore causing a rapid flaking of the protective layer. The deposition processes are largely known, as are their operating parameters, e.g. from DE-A-1496809, DE-A-1521079, FR-A-1301720 and vol. 92 of Chemical Abstracts, 1980, page 504, no. 118542f citing the Japanese patent application JP-A-79117335. They are usually performed in electrolytic baths of sulphate in aqueous solution, in the presence of chromium dioxide, with lead anodes and cathodes, constituted by the work pieces to be covered, with a current density lying between 10 and 30 Ampere/dm² and a speed of deposition of about 20—25 µm/h.

Known electro-deposition processes are not entirely free from disadvantages. In particular they permit coating layers of only a small thickness which are not suitable to ensure a long life of the elements treated, which is necessary, on the other hand to be able to extend the maintenance intervals of the engines fitted with such elements. Further, there is a tendency these days, for reasons of economy, to use inferior fuels, rich in sulphur and other corrosive elements and which therefore cause a rapid corrosive wear of the protective layers, whether obtained by electro-deposition methods or with other methods, and of the elements protected thereby.

An object of the present invention is that of providing a process for obtaining a protective coating for surfaces subjected to wear, which will be free from the described disadvantages and in particular of greater thickness and resistance to chemical corrosion so as to be able effectively to protect the surfaces to which they are applied.

Another object of the present invention is that of providing such a protective coating by utilising electro-deposited coating layers.

The said objects are achieved by the present invention in that it relates to a process for obtaining a protective coating for metallic surfaces subjected to wear by sliding and oxidation, in particular for metallic surfaces of elements of heat engines, comprising a first electro-deposition phase depositing onto the said surfaces a first layer of hard chrome, and a second electro-deposition phase depositing onto the said first layer of hard chrome a second layer of hard chrome, characterized in that said first electro-deposition phase is carried out in an aqueous electrolytic bath containing CrO₃ and chromic acid having such a composition to ensure a final hardness (Vickers) of said first layer lying between 400 and 600 kg/mm², said first electro-deposition phase being carried out with a current density of substantially 30 Ampere/dm² associated with a deposition speed comprised between 5 and 15 µm/h and with a voltage between the electrodes of between 4 and 10 volts until a thickness of said first layer lying between 20 and 40 µm is reached; and being further characterized in that said second electro-deposition phase is carried out in an aqueous electrolytic bath containing CrO₃ and a mixture of sulphuric and hydro-fluoric acid, having such a composition to ensure a final hardness (Vickers) of said second layer equal to or greater than 1000 Kg/mm²; said second electro-deposition phase being carried out with a current density comprised between 40 to 70 Ampere/dm² associated with a deposition speed of four to ten times greater than the speed of deposition of chrome in the said first phase, the voltage between the electrodes being comprised between 5 and 15 Volts, said second electro-deposition phase being carried out until a maximum thickness of said second layer of 1.2 mm is reached.

The present invention further relates to a protective coating for covering metallic surfaces subjected to thermal and mechanical wear of elements of heat engines, in particular for elements constituting the combustion chamber of a diesel engine and particularly for piston rings and piston sealing rings of reciprocating engines, said coating comprising a first layer of electro-deposited hard chrome, and a second layer of electro-deposited hard chrome, superimposed to said first layer, characterized in that said first layer has a thickness comprised between 20 and 40 µm and a hardness lying between 400 and 600 HV, and is substantially compact; in combination with such characteristics said second layer having a hardness of at least 1000 HV and a maximum thickness of 1.2 mm, said second layer being further pro-

vided with a plurality of micro-cracks dispersed uniformly therein and having dimensions lying between 5 and 30 μm and a distribution frequency in the second layer of at least about 200 micro-cracks per linear cm.

For a better understanding of the present invention a non-limitative embodiment thereof will be described with reference to the attached drawings, in which:

Figure 1 illustrates a photograph on an enlarged scale of a section of a sealing ring for heat engine pistons, provided with a protective coating formed according to the invention;

Figure 2 illustrates a micro-photograph enlarged 500 times, of a base zone of the coating of Figure 1;

Figure 3 illustrates a micro-photograph enlarged 500 times, of an intermediate zone of the coating of Figure 1; and

Figure 4 illustrates a photograph on an enlarged scale of a section of a sealing ring such as in Figure 1, but provided with a protective coating formed with a known process.

With reference to Figure 1, an element of a combustion chamber for a heat engine is generally indicated 1, this being constituted, in the illustrated example, by a sealing ring for a diesel engine piston. The element 1, of which, for simplicity, only an outer portion of the radial section is illustrated, has a surface 2, in the illustrated example the outer side surface, subjected to wear both by sliding and oxidation, being intended to form a sliding seal between piston and the side wall of the cylinder of an engine in operating conditions. The surface 2 is provided with a protective coating 3 which acts to protect it both from mechanical wear and from thermal wear due to chemical and electro-chemical attack at high temperature by the combustion products.

The protective coating 3, in the illustrated example, comprises two superimposed layers, electro-deposited onto the surface 2; a first layer 4 of hard chrome, having a Vickers hardness of 536 Kg/mm^2 and a thickness of 35 μm (0.035 mm) deposited immediately in contact with the surface 2 of the element 1, which is made of cast iron; and a second layer 5 of hard chrome, having a Vickers hardness of 1073 Kg/mm^2 (1073 HV) and of thickness equal to 1.05 mm, deposited over the layer 4. As can be seen in Figures 2 and 3, the layer 4 is compacted, substantially free from cracks, micro-cracks and porosity, and adheres perfectly to the cast iron of the element 1. The layer 5 is perfectly adherent to the layer 4, free from blow holes and cracks, well formed and having instead a plurality of micro-cracks 6 of very small dimensions (Figure 3) lying between about 5 and 30 micron, uniformly distributed in the layer 5 itself.

More generally, the protective coating 3 formed according to the invention can be applied to any surface subject to thermal and mechanical wear, and in the field of engines not only the piston rings, but also the valve stems and the cylinder

sleeves, and the piston crowns or cavities can be covered with this coating. The coating 3 can be made with a number of different variants, depending on technical requirements of the various applications, and therefore the layer 4 has a thickness lying between 20 and 40 μm and a hardness lying between 400 and 600 HV, while the layer 5 can have a hardness equal to or greater than 1000 HV and a maximum thickness equal to 1.2 mm. In a variant not illustrated the coating 3 further comprises a third electro-deposited layer for running in made of hard chrome deposited over the layer 5, of a hardness lying between about 650 and 800 HV and having a thickness such as to be completely worn away, leaving the layer 5 exposed, during the running-in phase of the engine the elements of which have had the coating 3 applied thereto.

The coating 3 has the dual function of constituting a protective layer for the surface 2 with regard to oxidising and chemically aggressive agents in general, and constitutes a consumable anti-wear layer for the surface 2. According to the invention this dual function is performed separately by the two layers 4 and 5. The layer 4, thanks to its high compactedness and excellent adhesion to the base material, whether it be cast iron or steel, guarantees the anti-corrosive and anti-oxidative protection even in the presence of high temperatures (such as, for example, those in the combustion chambers of super-charged engines) and aggressive fuels such as heavy diesel having a high sulphur content. Thanks to its high thermal stability and to its capacity for rapid passivation, in fact, the chrome layer 4 prevents the formation of local electro-chemical corrosion pairs and the penetration of corrosive agents towards the base material.

The layer 5, on the other hand, serves to be slowly consumed during the operating life of the element 1 in such a way as to prevent direct sliding of the surface 2 and consequent possible gripping or seizure. Thanks to the great thickness (more than three times the normal thickness of electro-deposited chrome protective layers) it allows about three times the operating life of the element 1 permitting the maintenance intervals of the engines on which the elements provided with protective coatings 3 are fitted to be extended. One characteristic of this layer 5, as well as its thickness, is represented by the presence of the micro-cracks 6. These have dimensions such as to be able to collect and retain lubricating oil in such a way as to allow the formation of an internal oil reserve in the layer 5, which can be used in the event of critical lubrication conditions preventing any risk of seizure or damage to the protective coating 3. Experimental tests have verified that improved results of durability and adequacy of lubrication are obtained when the distribution frequency of the micro-cracks in the layer 5 is equal to or greater than about 200 micro-cracks per linear cm, which represents a critical value.

The protective coating 3 previously described is obtained with the following process.

After having proceeded with an accurate cleaning of the element 1 to be coated, there is deposited on the surface 2, by means of electro-deposition treatment, the layer 4 by operating in an electrolytic vessel with lead anodes and cathodes constituted by the elements to be coated, in an electrolytic bath containing chrome in solution, preferably as CrO_3 , and chromic acid and with a voltage between the electrodes of between 4 and 10 volts. To obtain a layer 4 having the characteristics described, and therefore high compactedness, free from cracks and porosity, with good adhesion to the base metal, it is necessary however to operate in conditions with particular operating parameters, selected following a long experimenting period which has permitted, surprisingly, layers of electro-deposited chrome having the said characteristics to be obtained and which can be deposited with excellent adhesion directly on the base metal (cast iron or steel), without the inter-position of an anchoring layer of nickel. These operating parameters consist in a high cathode current density of substantially 30 Ampere/dm², associated with a very slow deposition speed lying between about 5 and 15 $\mu\text{m}/\text{hour}$. The combination of these values allows an electro-crystallisation process to be obtained for the deposition, characterised by the presence of a very large number of nuclei of crystallisation and by crystals of very small dimensions; this permits the best characteristics of compactedness and adhesion of the chromium deposits to be obtained, which results in total impermeability to corrosive agents.

The hardness and thickness of the layer 4 can instead be chosen in dependence on the single coating requirements, by varying in a known way the duration of the deposition operation and the percentage composition of chrome in the bath; these must however remain between the following values:

—thickness of the layer 4:

20—40 μm

—Vickers hardness of the layer 4:

400—600 Kg/mm²

After having obtained the layer 4 a washing operation is performed and then a second electro-deposition operation, this time utilising an aqueous electrolytic bath containing CrO_3 and a mixture of acids based on sulphuric acid (H_2SO_4) mixed with hydrofluoric acid (HF) and possibly with other mineral acids.

The chrome layer 5 is deposited after the layer 4, acting in vessels with lead anodes and cathodes constituted by the elements to be treated and a voltage between the electrodes of about 5—15 volts. To obtain a great thickness of the layer 5, equal to more than three times the normally obtainable thickness, and simultaneously obtain a regular and compacted deposit, provided with micro-cracks 6, it has, surprisingly, been found that it is necessary to operate with an unusually high cathode current density, lying between 40 and 70 Ampere/dm² in combination with a speed of deposition which is

also high, between four and ten times greater than the speed used for depositing the layer 4 and lying between 40 and 80 μm per hour. In this case, too, by varying the composition of the bath in a known way the hardness of the deposit, which must be greater than or equal to 1000 Kg/mm² (Vickers) can be determined. The maximum economic thickness of the layer 5 is of the order of 1.2 mm.

Optionally, a further electro-deposition operation can subsequently be performed by depositing on the layer 5 a further hard chrome layer of Vickers hardness lying between 650 and 800 Kg/mm² by working with a cathode current density of about 30—40 Ampere and a speed of deposition equal to that used in the deposition phase of the layer 5. This produces a layer having characteristics similar to those of the layer 5 but somewhat softer, which can be used as a running-in layer. Micro-cracks 6 can also be obtained in this layer.

From what has been described the advantages of the process according to the invention will be apparent. It allows chrome protective coatings of a new concept and very high characteristics of strength and durability to be obtained. Above all, the process described allows a chrome protective coating layer of great thickness to be obtained (a thickness greater than three times the thickness of current layers) in times substantially equal to those necessary to obtain conventional layers (of smaller thickness) with known processes, thanks to the high speed of deposition which is about three times that normally used. From a comparison between the photographs of Figures 1 and 4, respectively illustrating two electro-deposited chrome layers 5 of equal thickness, the first (Figure 1) deposited on a base layer 4 of pure chrome and with the process of the invention, and the second (Figure 4) with a conventional process onto a base layer of nickel, one can see how the chrome layer of Figure 4, because of the great thickness, has numerous macroscopic cracks which would in use lead to a rapid flaking of the layer itself.

Claims

1. A process for obtaining a protective coating (3) for metallic surface (2) subjected to wear by sliding and oxidation, in particular for metallic surfaces (2) of elements (1) of heat engines, comprising a first electro-deposition phase depositing onto the said surfaces (2) a first layer (4) of hard chrome, and a second electro-deposition phase depositing onto the said first layer (4) of hard chrome a second layer (5) of hard chrome, characterized in that said first electro-deposition phase is carried out in an aqueous electrolytic bath containing CrO_3 and chromic acid having such a composition to ensure a final hardness (Vickers) of said first layer (4) lying between 400 and 600 Kg/mm², said first electro-deposition phase being carried out with a current density of substantially 30 Ampere/dm² associated with a deposition speed comprised between 5 and 15

µm/h and with a voltage between the electrodes of between 4 and 10 volts until a thickness of said first layer lying between 20 and 40 µm is reached; and being further characterized in that said second electro-deposition phase is carried out in an aqueous electrolytic bath containing CrO₃ and a mixture of sulphuric and hydrofluoric acid, having such a composition to ensure a final hardness (Vickers) of said second layer (5) equal to or greater than 1000 Kg/mm²; said second electro-deposition phase being carried out with a current density comprised between 40 to 70 Ampere/dm² associated with a deposition speed of four to ten times greater than the speed of deposition of chrome in the said first phase, the voltage between the electrodes being comprised between 5 and 15 Volts, said second electro-deposition phase being carried out until a maximum thickness of said second layer of 1.2 mm is reached.

2. A process according to Claim 1, characterised by the fact that it further includes a third phase, subsequent to the said second phase, comprising electro-deposition of a third layer of hard chrome of Vickers hardness lying between about 650 and 800 Kg/mm², said third layer being deposited onto said second layer (5) operating such as in said electro-deposition phase, but with a current density comprised between 30 and 40 Ampere/dm².

3. A protective coating (3) for covering metallic surfaces (2) subjected to thermal and mechanical wear of elements (1) of heat engines, in particular for elements (1) constituting the combustion chamber of a diesel engine and particularly for piston rings and piston sealing rings of reciprocating engines, said coating (3) comprising a first layer (14) of electrodeposited hard chrome, and a second layer (5) of electrodeposited hard chrome, superimposed to the said first layer (4), characterized in that said first layer (4) has a thickness comprised between 20 and 40 µm and a hardness lying between 400 and 600 HV, and is substantially compact; in combination with such characteristics said second layer (5) having a hardness of at least 1000 HV and a maximum thickness of 1.2 mm, said second layer (5) being further provided with a plurality of micro-cracks dispersed uniformly therein and having dimensions lying between 5 and 30 µm and a distribution frequency in the said second layer of at least about 200 micro-cracks per linear cm.

4. A coating (3) according to Claim 3, characterised by the fact that it further includes a third layer of hard chrome overlying the said second layer (5) and having a hardness lying between about 650 and 800 HV, having a thickness such as to wear completely during the running-in phase of the said heat engines.

Patentansprüche

1. Verfahren zum Herstellen eines Schutzüberzuges (3) für Metallflächen (2), die durch Gleiten und Oxidation Abnutzung unterliegen, insbesondere für Metallflächen (2) von Elementen (1) von

Wärmekraftmaschinen, umfassend eine erste elektrolytische Fällungsphase, die auf diesen Oberflächen (2) eine erste Schicht (4) aus Hartchrom abscheidet, und eine zweite elektrolytische Fällungsphase, die auf diese erste Schicht (4) aus Hartchrom eine zweite Schicht (5) aus Hartchrom abscheidet, dadurch gekennzeichnet, daß die erste Elektrolytische Fällungsphase in einem wässrigen Elektrolysebad enthaltend CrO₃ und Chromsäure mit einer solchen Zusammensetzung, daß eine Endhärte (Vickers) der ersten Schicht zwischen 400 und 600 kg/mm² gewährleistet ist, durchgeführt wird, wobei die erste elektrolytische Fällungsphase mit einer Stromdichte von im wesentlichen 30 Ampere/dm² in Verbindung mit einer Abscheidungsgeschwindigkeit von 5 bis 15 µm/h und mit einer Spannung zwischen den Elektroden von 4 bis 10 Volt durchgeführt wird, bis eine Dicke der ersten Schicht zwischen 20 und 40 µm erreicht ist, und weiter dadurch gekennzeichnet, daß die zweite elektrolytische Fällungsphase in einem wässrigen Elektrolysebad, das CrO₃ und eine Mischung von Schwefel- und Fluorwasserstoffsäure enthält, mit einer derartigen Zusammensetzung, daß eine Endhärte (Vickers) der zweiten Schicht (5) gleich oder größer als 1000 kg/mm² gewährleistet ist, durchgeführt wird, wobei die zweite elektrolytische Fällungsphase mit einer Stromdichte von 40 bis 70 Ampere/dm² in Verbindung mit einer Abscheidungsgeschwindigkeit, die vier- bis zehnmal höher ist als die Geschwindigkeit der Abscheidung des Chroms in der ersten Phase, durchgeführt wird, wobei die Spannung zwischen den Elektroden 5 bis 15 Volt beträgt, welche zweite elektrolytische Fällungsphase durchgeführt wird, bis eine maximale Dicke der zweiten Schicht von 1,2 mm erreicht ist.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß es weiters eine dritte Phase anschließend an diese zweite Phase aufweist, die die elektrolytische Fällung einer dritten Schicht aus Hartchrom mit einer Vickers-Härte von etwa 650 bis 800 kg/mm² umfaßt, wobei die dritte Schicht auf die zweite Schicht (5) abgeschieden wird und wobei wie in der genannten elektrolytischen Fällungsphase, jedoch mit einer Stromdichte zwischen 30 und 40 Ampere/dm² gearbeitet wird.

3. Schutzüberzug (3) zum Überziehen von Metallflächen (2), die thermischer und mechanischer Abnutzung von Elementen (1) von Wärmekraftmaschinen unterliegen, insbesondere für Elemente (1), die die Verbrennungskammer eines Dieselmotors bilden, und insbesondere für Kolbenringe und Kolbendichtungsringe von Kolbenkraftmaschinen, welcher Überzug (3) eine erste Schicht (14) aus elektrolytisch gefälltem Hartchrom und eine zweite Schicht aus elektrolytisch gefälltem Hartchrom, die auf die erste Schicht (4) aufgebracht ist, umfaßt, dadurch gekennzeichnet, daß die erste Schicht (4) eine Dicke von 20 bis 40 µm und eine Härte von 400 bis 600 HV aufweist und im wesentlichen kompakt ist, wobei in Kombination mit derartigen Merkmalen die zweite

Schicht (5) eine Härte von mindestens 1000 HV und eine maximale Dicke von 1,2 mm aufweist, welche zweite Schicht (5) weiters mit einer Vielzahl von gleichförmig darin verteilten Mikrorissen mit Dimensionen von 5 bis 30 μm und einer Verteilungsfrequenz in dieser zweiten Schicht von mindestens etwa 200 Mikrorissen pro linearem cm versehen ist.

4. Überzug (3) nach Anspruch 3, dadurch gekennzeichnet, daß er weiters eine dritte Schicht aus Hartchrom aufweist, die über der zweiten Schicht (5) liegt, mit einer Härte von etwa 650 bis 800 HV und einer derartigen Dicke, daß sie während der Einlaufphase der Wärmekraftmaschinen vollständig abgerieben wird.

Revendications

1. Procédé pour obtenir un revêtement de protection (3) pour des surfaces métalliques (2) soumises aux contraintes par glissement et oxydation, en particulier pour des surfaces métalliques (2) d'éléments (1) de moteurs thermiques, comprenant une première phase d'électro-déposition sur lesdites surfaces (2) d'une première couche (4) en chrome dur, et une seconde phase d'électro-déposition sur ladite première couche (4) en chrome dur d'une seconde couche (5) en chrome dur caractérisé en ce que ladite première phase d'électro-déposition est réalisée dans un bain électrolytique aqueux contenant du CrO_3 et de l'acide chromique présentant une composition telle qui assure une dureté finale (Vickers) de ladite première couche (4) comprise entre 400 et 600 kg/mm^2 , ladite première phase d'électro-déposition étant réalisée avec un courant de densité de pratiquement 30 A/dm^2 associée à une vitesse de déposition comprise entre 5 et 15 μh et avec une tension entre les électrodes comprise entre 4 et 10 V jusqu'à ce que l'épaisseur de ladite première couche comprise entre 20 et 40 μ soit atteinte; et, en outre, en ce que ladite seconde phase d'électro-déposition est réalisée dans un bain électrolytique aqueux contenant du CrO_3 et un mélange d'acide sulfurique et fluorhydrique présentant une composition telle qui assure une dureté finale (Vickers) à ladite seconde couche (5) égale ou supérieure à 1000 kg/mm^2 ; ladite seconde phase de déposition par électrolyse étant réalisée avec une densité de courant comprise entre 40 et 70 A/dm^2 associée à une vitesse de

déposition supérieure à 4 ou 10 fois la vitesse de déposition du chrome dans ladite première phase, la tension entre les électrodes étant comprise entre 5 et 15 V, ladite seconde phase d'électro-déposition étant réalisée jusqu'à ce qu'une épaisseur maximale de 1,2 mm de ladite seconde couche soit atteinte.

2. Procédé selon la revendication 1 caractérisé en ce qu'il comporte une troisième phase, postérieure à ladite seconde phase, comprenant une électro-déposition d'une troisième couche en chrome dur de dureté Vickers comprise entre environ 650 et 800 kg/mm^2 , ladite troisième couche étant déposée sur ladite seconde couche (5) agissant comme dans ladite seconde phase d'électro-déposition mais avec une densité de courant compris entre 30 et 40 A/dm^2 .

3. Revêtement de protection (3) pour recouvrir les surfaces métalliques (2) soumises aux contraintes mécaniques et thermiques, en particulier pour des éléments (1) constitutifs de la chambre de combustion d'un moteur diesel et particulièrement pour des segments de piston et des segments d'étanchéité de piston de moteurs réciproques, ledit revêtement (3) comprenant une première couche (4) en chrome dur électro-déposée, et une seconde couche (5) en chrome dur électro-déposée superposée sur ladite première couche (4) caractérisé en ce que ladite première couche (4) présente une épaisseur comprise entre 20 et 40 microns et une dureté comprise entre 400 et 600 HV, et est pratiquement compacte; en combinaison avec de telles caractéristiques de ladite seconde couche (5) présentant une dureté d'au moins 1000 HV et une épaisseur maximale de 1,2 mm, ladite seconde couche (5) étant en outre munie d'une pluralité de micro-fissures dispersées uniformément à l'intérieur et présentant des dimensions comprises entre 5 et 30 μ et une répartition de distribution dans ladite seconde couche d'au moins environ 200 microfissures par cm.

4. Revêtement (3) selon la revendication 3 caractérisé en ce qu'il comporte, en outre, une troisième couche en chrome dur recouvrant ladite seconde couche (5) et présentant une dureté comprise entre environ 650 et 800 HV, et une épaisseur telle qu'elle soit complètement usée lors de la période de rodage desdits éléments des moteurs thermiques.

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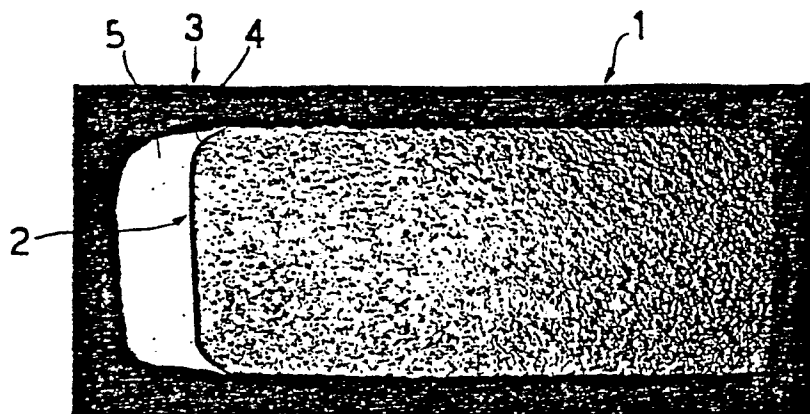


Fig. 1

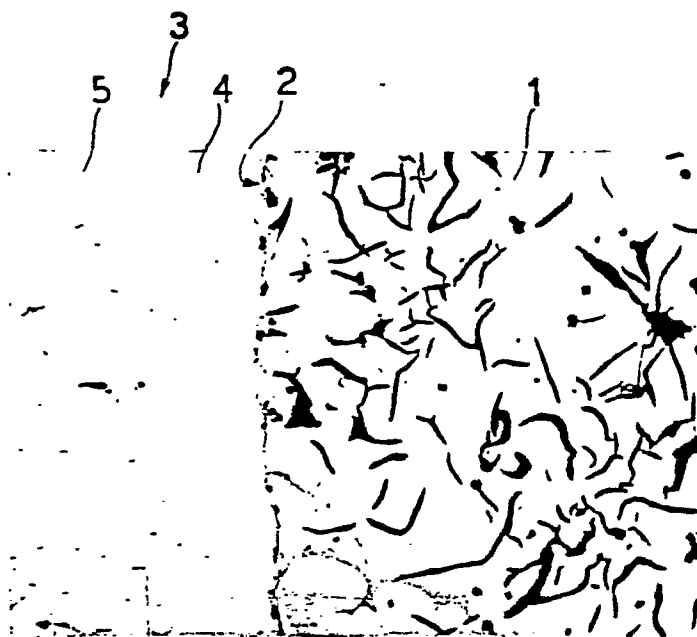


Fig. 2

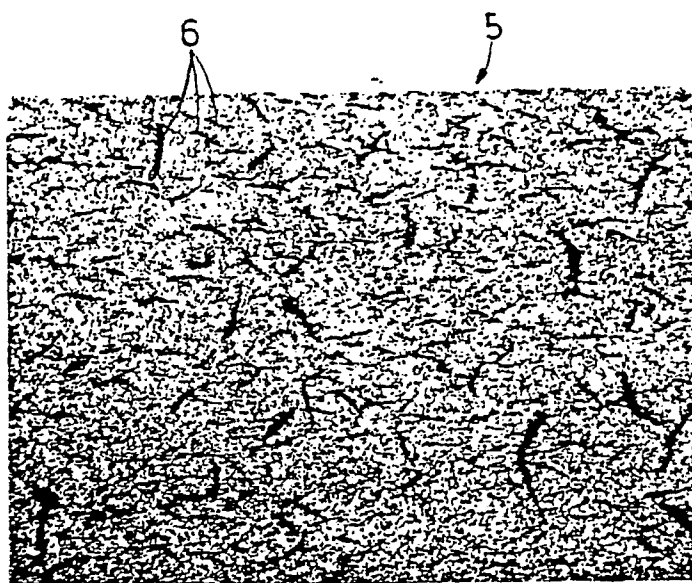


Fig. 3

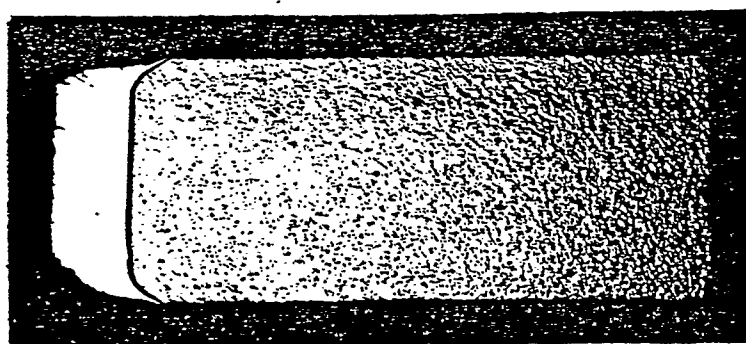


Fig. 4