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(54) Process for producing multilayer coating with high abrasion resistance

(57) Procedure to obtain multilayer coatings with high wear resistance, in particular for light alloy metal materials and for metal matrix composite materials, wherein the material to be coated is subjected to the following operations: a) surface deposition, using thermal spray techniques, of a first cermet coating, with thickness ranging from 20 to 600 µm; b) surface finishing treatment; c) deposition on the first coating, using vapour phase deposition techniques, of a second nitride or carbon coating, with thickness ranging from 1 to 10 µm.

EP 1 548 153 A2

Description

Field of the invention

[0001] The present invention relates to a procedure to obtain, by means of combined thermal spray and vapour phase deposition techniques, a multilayer coating capable of improving the wear resistance of light alloy metal materials and metal matrix composite materials.

State of the art

[0002] Wear of the material, which can be defined as ablation of material due to interaction between surfaces in relative motion, is the greatest cause of the reduction and the loss of performance in mechanical and machine couplings, and therefore any decrease in this phenomenon is considered advantageous.

[0003] The phenomenon of wear, which includes all phenomena that cause damage on the surface of two solid bodies which are in contact with each other and in relative movement, is produced in the following ways.

[0004] According to a first way, subsequent to rubbing between solid bodies the layer of surface coating can become damaged and detach (due to friction), and in this case wear is the result of adhesion between the coatings of the bodies and is called adhesion wear.

[0005] In a second way, when the surface guarantees partial resistance to modest forms of wear, fatigue processes can arise due to stress cycles which occur during rubbing or rolling, this type of phenomenology is called wear fatigue.

[0006] In a third mode, if one of the two materials in contact is constituted by very hard particles (but also if it is coated with a film of very hard particles) without the other being adequately protected, a form or wear known as abrasive wear, which at times is very rapid, occurs.

[0007] The way with which wear is produced is determined mostly by the characteristics of the material and by the operating conditions. For metals there can generally be two cases:

- in the absence of lubrication, the wear of metals or other oxidizable solids takes place by cyclic fragmentation of the oxide film and subsequent reformation thereof;
- in the presence of lubrication, wear takes place by fatigue with the formation of surface cracks and possibly wear particles detached from the surface.

[0008] With equal test conditions, when there is a variation in the maximum load applied, for example in the presence of a reduction thereof, there is an opposite variation in the number of cycles required for breakage, in this case an increase. The correlation between maximum load applied and the number of cycles required to break the piece is summarized in the Woehler curve.

[0009] In the current state of evolution of technology, to improve resistance to wear and to mechanical fatigue of components subject to cyclic loading, various solutions are adopted:

a) improvement in the design, with elimination or improvement of the points in which stress is concentrated,
b) increase in the dimensions of the component to reduce the applied load;
c) reduction in applied stress;
d) replacement of the material with a material with greater resistance to mechanical fatigue;
e) improvement in the surface finish by mechanical machining processes or other expedients; and
f) creation of protective coatings and/or surface layers in compression by applying techniques such as shot blasting or rolling.

[0010] Particularly favourable situations for the onset of wear phenomena are found in ring gears of cycles and motorcycles that use a chain to transmit motion.

[0011] Currently the transmission gears for motorcycles are made of steel and light aluminium alloy type AA7075, the production of Ti gears implies rapid deterioration caused by fretting fatigue and the production of Mg gears implies insufficient mechanical properties, for example hardness and yield, which are much lower than the properties of aluminium alloy alone.

[0012] Attempts have been made to use surface coatings to solve the problems indicated by providing a solution to reduce wear of the light alloy gears for motorcycle use and simultaneously increase the mechanical properties of the layer of surface material.

[0013] The application of hard wear-resistant coatings to light alloys and metal matrix composite materials is generally a critical process due to the considerable difference in the mechanical properties of the substrate material and of the facing material. The mechanical and point stresses can easily cause breakage of the hard surface coatings with consequent damage to the coated material.

[0014] Notwithstanding numerous efforts made to date, the state of the art technologies available still have many drawbacks in technological and economic terms and there are no optimal coatings; therefore it is highly desirable to obtain better protective coatings to those currently known.

Summary of the invention

[0015] The object of the present invention is to provide a procedure to improve wear resistance of light alloy metal materials or metal matrix composite materials, by application of a suitable multilayer coating on the surface thereof, capable of locally improving the characteristics of resistance of the component and therefore reducing the formation and expansion of cracks. The phenomenon on which the increase in performance of components is based consists of producing a multilayer facing, with gradually increasing hardness, from the substrate to the surface.

[0016] These objects, and others which shall become apparent by reading the description hereunder, are obtained in conformity with the main object of the present invention using a procedure to produce a multilayer coating with high wear resistance for metal materials with the characteristics of claim 1. in particular, it is advantageously applied to light alloy materials and to metal matrix composite materials. The material to be coated is substantially subjected to the following operations: surface deposition, using thermal spray techniques, of a first cermet coating, with thickness ranging from 20 to 600 μm; surface finishing treatment; deposition on the first coating, using vapour phase deposition techniques, of a second nitride or carbon coating, with thickness ranging from 1 to 10 μm.

[0017] The surface finishing treatment according to the invention consists of mechanical machining chosen from the group comprising: polishing and/or lapping and/or grinding and/or shot blasting and/or combinations thereof.

[0018] In particular embodiments of the procedure, the surface can also be prepared prior to the procedure of the invention and, if necessary, stabilizing heat treatment is carried out, at a temperature ranging from 20 and 800°C. Surface preparation consists. for example, of a treatment chosen from the group comprising: mechanical and/or electrolytic and/or chemical cleaning and/or combinations thereof.

[0019] Moreover, in a further particular embodiment, the stage of diffusion and annealing at 700-750°C for 10 hours in a protective atmosphere is performed immediately after cermet coating.

[0020] The thermal spray techniques according to the invention are preferably chosen from the group comprising: CAPS (Controlled Atmosphere Plasma Spray), HVOF (High Velocity Oxy Fuel), VPS (Vacuum Plasma Spray) and combinations thereof. The thermal spray techniques are applied at a temperature ranging from 50 to 350°C.

[0021] The cermet material used for thermal spray coating is chosen from the group comprising carbide, oxide or nitride dispersions, chosen from the group comprising WC, TiC, CrC, Al_2O_3, TiO2, TiN, CrN, in metal matrices, chosen from the group comprising Co, NiCr, NiCrFeBSi, NiAl, Mo, NiCoCrAlY, Ti alloys.

[0022] Vapour phase deposition techniques according to the invention are chosen from the group comprising PVD or CVD and are preferably chosen from the group comprising: Arc-PVD, Sputtering PVD, Electron Beam PVD, CVD, also in the respective Plasma Assisted variants.

[0023] The material used for the coating obtained by vapour phase deposition is chosen from the group: TiN, CrN, ZrN, TiCN, TiAlN, DLC, in simple form or obtained from the combination in succession of two or more of these materials.

[0024] The metal material is chosen from the group comprising: aluminium alloy, titanium alloy, magnesium alloy.

[0025] The deposition temperature of the thermal spray coating, in the case in which the metal material is aluminium alloy, ranges from 80-300°C and is preferably 150°C.

[0026] The deposition temperature of the thermal spray coating, in the case in which the metal material is titanium alloy, ranges from 70-400°C and is preferably 150°C.

[0027] The metal matrix composite material is chosen from the group comprising: a matrix of Aluminium, Titanium, Magnesium, Copper, Lead, Iron or Silver reinforced with Alumina, Graphite, Silicon Carbide, Titanium Boride or Boron.

[0028] A further object of the present invention is the multilayer coating with high resistance to wear for light alloy metal materials and for metal matrix composite materials obtainable with the procedure indicated.

[0029] The present invention is used in all those cases which require the presence of components subject to cyclic application of mechanical loads, for example for applications in the aerospace, aeronautical, transport, mechanical components sectors and the like.

[0030] A possible example of application of the present invention is in the aircraft, car, motorcycle and bicycle components sector, for example to produce ring gears, and in any case all those components in which it is important to reduce weight and/or cost.

[0031] As non-ferrous alloys, and in particular light alloys, such as aluminium, do not have a fatigue limit '(that is, it is impossible to define for these a load with a value below which we are certain that fatigue breakage will not occur under cyclic loading) it is necessary to guarantee oversizing of the piece or to use stronger, but heavier materials such as steels, or more costly materials, such as titanium alloy. This causes an increase in the weight and/or cost of the component. instead, by adopting the invention, the weight and cost of the pieces can be decreased, both by reducing the dimensions and by using light alloys, which thanks to the procedure according to the invention, can benefit from a considerable increase in resistance to wear and to surface fatigue, even of low strength alloys.

[0032] The dependent claims describe preferred embodiments of the invention.

Brief description of the Figures

[0033] Further characteristics and advantages of the invention shall be more apparent in the light of the detailed description of preferred, although non-exclusive, embodiments of a procedure to produce multilayer coatings with high resistance to wear, provided by way of non-limiting examples, with the aid of the accompanying drawings, in which:

Figure 1 represents the profile of a tooth of an aluminium gear in which the high rate of wear on the transmission side is highlighted;

Figure 2 shows a diagram of the deposition kinematics in the thermal spray procedure, in which the curvilinear arrow indicates the movement of the gear during coating and the straight arrows indicate the directions of incidence of the thermal spray torch;

Figure 3 shows the section of a tooth coated with thermally sprayed cermet;

Figure 4 shows a micrograph of a section of the multilayer coating composed of cermet and of the thin film approximately 3 μm thick according to the present invention.

Figure 5 shows a diagram of the specific resistance of the material;

Figure 6 shows the microstructure of the area reinforced by the procedure of the invention in a particular application.

Detailed description of preferred embodiments of the invention

[0034] Specific embodiments of the procedure for producing multilayer coatings with high resistance to wear are now described with particular reference to practical applications.

EXAMPLE 1

[0035] A ring gear for motorcycle applications is indicated as the first example of embodiment and has been produced on a substrate consisting of aluminium alloy AA7075. A surface preparation consisting of abrasive blasting was performed on this substrate.

[0036] A layer of chromium carbide cermet material in NiCr matrix was deposited on this substrate using the HVOF thermal spray procedure.

[0037] The layer of thermally sprayed cermet material produced has a thickness ranging from 50-300 μm. The material coated with cermet was subjected to a surface finishing treatment consisting of polishing. Finally, a CrN film, with a thickness of 3 μm, was deposited on the surface of the material using Arc-PVD technology.

[0038] Microstructure characterization of the multilayer coating highlighted the following results: absence of unmelted particles in the cermet layer; porosity below 0.5% in the cermet layer; good degree of homogeneity of the facing along the thickness; absence of cracks; excellent adhesion of the thermally sprayed facing to the Al alloy substrate and of the thin film to the cermet layer; absence of delamination between thin film and cermet coating.

EXAMPLE 2

[0039] A gear wheel for bicycle applications is indicated as the second example of embodiment and was produced on a substrate consisting of titanium alloy Ti6A14V. This substrate was subjected to surface preparation consisting of brushing, sanding and cleaning in an acetone ultrasound bath for 60 seconds. A layer of cermet, based on TiN dispersed in Ti matrix, was deposited on this substrate using the CAPS thermal spray technique at a temperature of 200°C. The layer of thermally sprayed cermet produced has a thickness ranging from 50-300 μm. The material coated with cermet was subjected to a surface finishing treatment consisting of grinding. Finally, a TiN film, 2 μm thick, was deposited on the surface of the material using Arc-PVD technology.

[0040] Microstructure characterization of the multilayer coating highlighted the following results: absence of unmelted particles in the cermet layer; porosity below 3% in the cermet layer; good degree of homogeneity of the facing along the thickness; absence of cracks; excellent adhesion of the thermally sprayed facing to the Ti alloy substrate and of the thin film to the cermet layer; absence of delamination between thin film and cermet coating.

[0041] The material thus obtained also improves the hot wear resistance thanks to the noteworthy reduction in porosity and cracks and, moreover, has a high level of hardness and toughness.

[0042] Tests were performed on these components with maximum load of 300 MPa applied to the outer layers, according to the following standard procedure: measurement of the minimum dimension; calculation of the flexural load corresponding to the maximum flexural stress of 300 MPa; application of the flexural load calculated by a balance system; start-up of the test; interruption of the test in the case of catastrophic fracture of the test piece. The results were compared by performing tests on two series of samples of the same geometry manufactured with the same Titanium alloy with and without coating. The results indicate that Titanium alloy as is has a considerably lower wear resistance than can be obtained with the procedure according to the present invention adopted in the example in question.

EXAMPLE 3

[0043] A pin or tubular dowel which connects the piston to the connecting rod of a combustion engine is indicated as the second example of embodiment and was produced using the Sheet-Fibre-Sheet technique "simultaneously rolling into a spiral" a mat of SCS-6 type commercial fibres superimposed on an ultra-thin sheet of titanium alloy, for example type Ti6Al4V, above an internal spindle. The internal spindle was subjected to pressure and made to expand on an external coaxial matrix. The final result is a hybrid cylinder with an area with high mechanical resistance in the region subjected to the greatest mechanical loading during the test. The specific mechanical properties are indicated in Figure 5.

[0044] In this way it is possible to optimize the cost of the component by inserting a composite insert with high mechanical properties in the area subjected to the most stress. An example of the microstructure of the reinforcing insert area is indicated in Figure 6.

[0045] A layer of cermet, based on CrC dispersed in a NiCr matrix, was deposited on this substrate using the HVOF thermal spray technique at a temperature of 150°C. The layer of thermally sprayed cermet material produced has a thickness ranging from 50-300 μm. The material coated with cermet was subjected to a surface finishing treatment consisting of grinding. Finally, a CrN film with a thickness of 2 microns, was deposited on the surface of the material using Arc-PVD technology.

[0046] Microstructure characterization of the multilayer coating highlighted the following results: absence of unmelted particles in the cermet layer; porosity below 3% in the cermet layer; good degree of homogeneity of the facing along the thickness; absence of cracks; excellent adhesion of the thermally sprayed facing to the composite material substrate and of the thin film to the cermet layer; absence of delamination between thin film and cermet coating.

Claims

1. Procedure for producing multilayer coatings with high wear resistance, in particular for light alloy metal materials and for metal matrix composite materials, **characterized in that** the material to be coated is subjected to the following operations:

   a) depositing on a surface of the material to be coated, by means of thermal spray techniques, of a first cermet coating with thickness ranging from 20 to 600 μm;
   b) applying a surface finishing treatment;
   c) depositing on the first coating, using vapour phase deposition techniques, a second nitride or carbon coating, with thickness ranging from 1 to 10 μm.

2. Procedure as claimed in claim 1, wherein the material to be coated is subjected to surface preparation prior to stage a).

3. Procedure as claimed in claim 2, wherein after surface preparation of the material to be coated and prior to stage a), stabilizing heat treatment is performed at a temperature ranging from 20 to 800°C.

4. Procedure as claimed in claim 1 or 3, wherein diffusion and annealing at 700-750°C for 10 hours in a protective atmosphere is performed between stage a) and stage b).

5. Procedure as claimed in claim 2, wherein the surface preparation consists of a treatment chosen from the group comprising: mechanical and/or electrolytic and/or chemical cleaning and/or combinations thereof.

6. Procedure as claimed in claim 1, wherein the surface finishing treatment consist of mechanical machining chosen from the group comprising: polishing and/or lapping and/or grinding and/or shot blasting and/or combinations thereof.

7. Procedure as claimed in any one of the previous claims, wherein the thermal spray techniques are preferably chosen from the group comprising: CAPS (Controlled Atmosphere Plasma Spray), HVOF (High Velocity Oxy Fuel), VPS (Vacuum Plasma Spray) and combinations thereof.

8. Procedure as claimed in any one of the previous claims, wherein said thermal spray techniques are applied at a temperature ranging from 50 to 350°C.

9. Procedure as claimed in any one of the previous claims, wherein the cermet material used for the first thermal spray coating is chosen from the group comprising carbide, oxide or nitride dispersions, chosen from the group comprising WC, TiC, CrC, Al_2O_3, TiO2,TiN, CrN, in metal matrices, chosen from the group comprising Co, NiCr, NiCrFeBSi, NiAl, Mo, NiCoCrAlY, Ti alloys.

10. Procedure as claimed in claim 1, wherein the vapour phase deposition techniques are chosen from the group comprising: PVD (Physical Vapour Deposition) or CVD (Chemical Vapour Deposition).

11. Procedure as claimed in claim 10, wherein the vapour phase deposition techniques are preferably chosen from the group comprising: Arc-PVD, Sputtering PVD, Electron Beam PVD, CVD, also in the respective Plasma Assisted variants.

12. Procedure as claimed in claim 11, wherein the material used for the second coating is chosen from the group: TiN, CrN, ZrN, TiCN, TiAlN, DLC (Diamond Like Carbon), in simple form or obtained from the combination in succession of two or more of these materials.

13. Procedure as claimed in any one of the previous claims, wherein the metal material to be coated is chosen from the group comprising: aluminium alloy, titanium alloy, magnesium alloy.

14. Procedure as claimed in any one of claims 1 to 13, wherein the metal material is aluminium alloy and the deposition temperature of the thermal spray coating ranges from 80-300°C.

15. Procedure as claimed in claim 14, wherein the deposition temperature of the thermal spray coating is 150°C.

16. Procedure as claimed in any one of claims 1 to 13, wherein the metal material is titanium alloy and the deposition temperature of the thermal spray coating ranges from 70-400°C.

17. Procedure as claimed in claim 16, wherein the deposition temperature of the coating is 150°C.

18. Procedure as claimed in any one of the previous claims, wherein said metal matrix composite material is chosen from the group comprising: a matrix of Aluminium, Titanium, Magnesium, Copper, Lead, Iron or Silver reinforced with Alumina, Graphite, Silicon Carbide, Titanium Boride or Boron.

19. Multilayer coating with high wear resistance for light alloy metal materials and for metal matrix composite materials, obtained using the procedure according to one or more of claims 1 to 18.

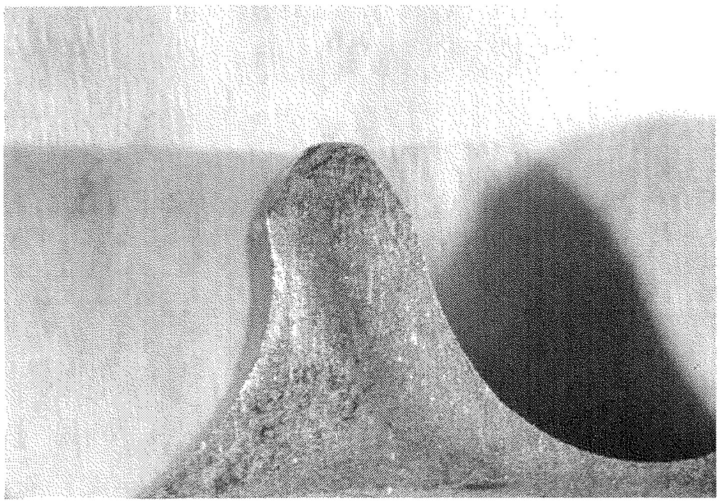

Fig. 1

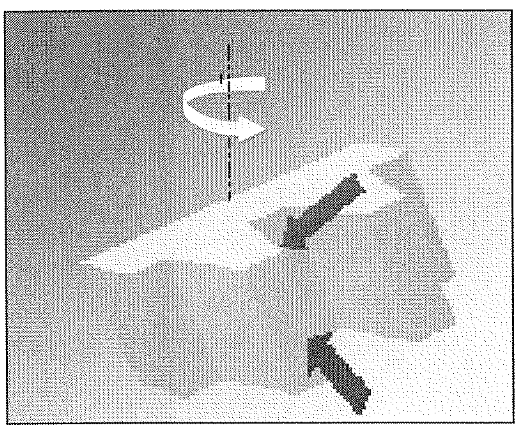

Fig. 2

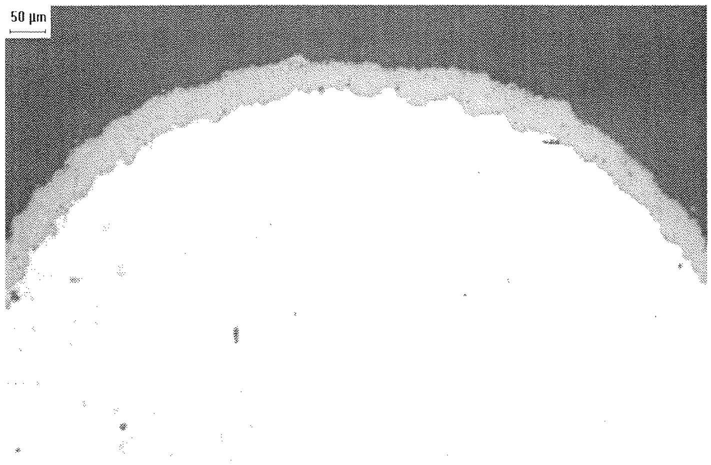

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Fig. 3

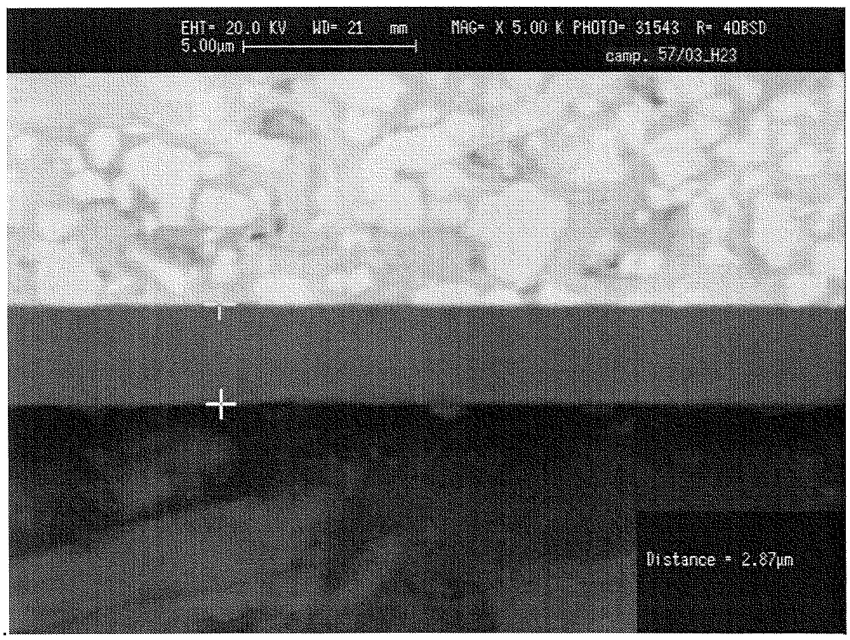


Fig. 4

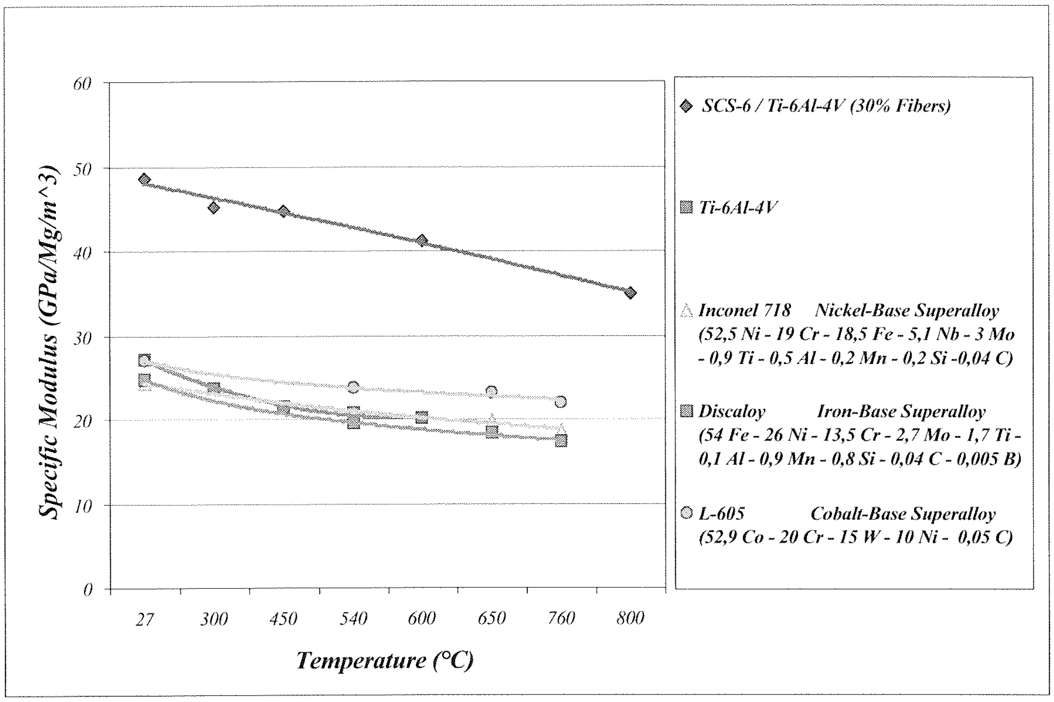
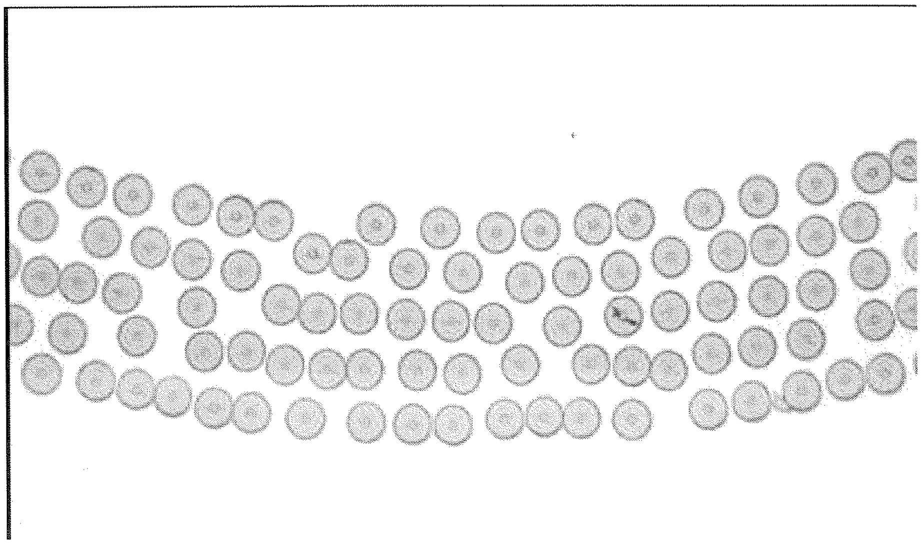


Fig. 5: Diagram of the specific resistance of the material



Fi g. 6: Microstructure of the area reinforced with the multilayer coating