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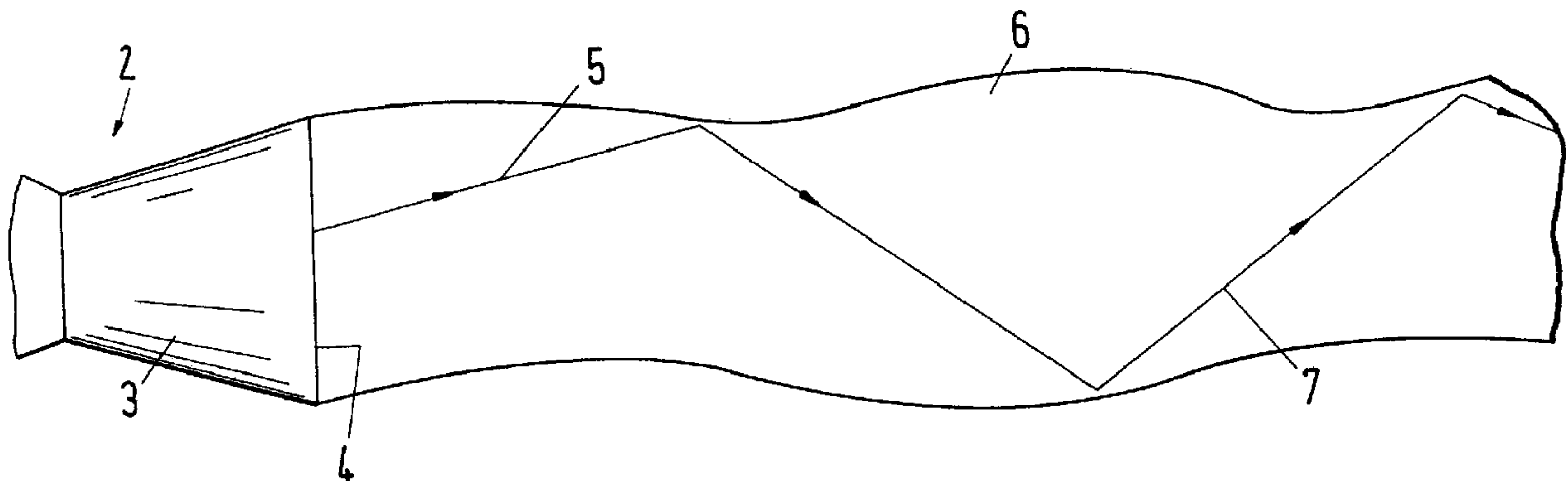
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(54) Titre : MATERIEL ET METHODE DE METALLISATION AU PISTOLET, ET REVETEMENT ET PIECE METALLISES AU PISTOLET

(54) Title: A THERMAL SPRAYING MATERIAL, A THERMALLY SPRAYED COATING, A THERMAL SPRAYING METHOD AND ALSO A THERMALLY COATED WORKPIECE



(57) Abrégé/Abstract:

The invention relates to a thermal spraying material (5) for the coating of a surface of a workpiece by means of a thermal spraying method, wherein the spraying material (5) contains zinc. The invention further relates to a thermal spraying method and to a thermally sprayed coating sprayed with the material (5).

Abstract of Disclosure

The invention relates to a thermal spraying material (5) for the coating of a surface of a workpiece by means of a thermal spraying method, wherein the spraying material (5) contains zinc. The invention further relates to a thermal spraying method and to a thermally sprayed coating sprayed with the material (5).

Fig. 2

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A thermal spraying material, a thermally sprayed coating, a thermal spraying method and also a thermally coated workpiece

The invention relates to a thermal spraying material, to the use of a material for the coating of a surface of a workpiece by means of a thermal spraying method, to a thermally sprayed coating, to a thermal spraying method and also to a thermally coated workpiece, as described herein.

The coating of surfaces of the most diverse workpieces has an almost incalculable number of uses in industrial technology and a correspondingly high economic significance. In this connection coatings can be advantageously applied to the most diverse substrates for very different reasons. Wear protection coatings on mechanically heavily loaded parts such as, for example, on running surfaces of cylinders or piston rings of combustion engines or compressors, play an important role for example. In addition to wear resistance further demands are made on these parts, such as good sliding characteristics, i.e. good tribological characteristics or also excellent dry operation characteristics. Different thermal spraying methods have in particular proved to be excellent for such requirements and similar ones, above all the known plasma spray methods.

Coatings manufactured by arc vaporisation, PVD or CVD processes have been used successfully for the production of hard layers on highly loaded tools, primarily chip-forming tools such as milling cutters, drills etc. How-

ever precisely the application of the last named processes is very widespread in completely different fields, for example for the coating of jewellery or clock housings or for the application of protective coatings or simply for the embellishment of basic commodities.

Other methods, such as for example gas nitriding, are well-established methods which are of great significance in corrosion protection, among other things.

In this connection the coating of workpieces with very large surface areas, such as metal sheets for example, which have to be protected against corrosion among other things, is fundamentally problematic. Metal sheets of this kind or other substrates are, for example, provided on rolls of a substantial width of up to a few metres and in a length of up to several hundred metres or even more.

An established technique for the coating of sheets of this kind is galvanic or electrolyte deposition, for example. Thus, it is known, for example, to provide large steel sheets with a corrosion protection layer made of Zn and Mg. In a typical known process a 1 μm to 30 μm thick layer made of pure zinc (Zn) is applied in a first step electrolytically or galvanically onto a metal sheet which can be, for example, be made of steel, of aluminium, of another metal or of a metal alloy. The surface of this first layer is then subjected to a cleaning process by means of ultrasound and/or PVD sputtering for example. After this a thin layer approximately 0.1 μm to 0.5 μm thick, made of pure magnesium (Mg) is applied to the first zinc layer by means of a PVD method. Finally, a heat treatment of the workpiece takes place for example for 10 min to 3 hours, at 200° C to 550° for example, in very special cases up to 650° C, through which diffusion processes are initiated, so that MgZn_2 phases can form on the surface of the originally pure

Mg layer, through which an improved protection against corrosion is attained.

The workpieces treated in this way have clearly improved corrosion characteristics in comparison to workpieces with pure zinc layers and can also be worked better because the combination layers as a whole have a reduced thickness. However, the above-described four-stage coating process is extraordinarily time-consuming and above all requires the combination of completely different methods, so that not only the carrying out of the coating process as such, but also machinery cost is enormous, so that the costs for the manufacture of these corrosion protection layers are basically unreasonably high

For these reasons alternatives have been sought for a long time, with thermal spraying in its different variants basically coming into question, primarily because thermal spraying has long been established in the series production of individual parts and industrial series production. The most usual thermal spraying methods, which are also used in particular in series production for the coating of the surfaces of substrates in large numbers are, for example, flame spraying with a spraying powder or a spraying wire, arc spraying, high velocity flame spraying (HVOF), flame detonation spraying or plasma spraying. The above-named list of thermal spraying methods is certainly not exhaustive. On the contrary the person averagely skilled in the art is familiar with a large number of variations of the listed methods, and also further methods, for example special methods such as flame spraying welding. The so-called "cold gas spraying" also has to be mentioned in this connection. Although, strictly speaking, it is not to be counted as one of the thermal spraying methods, within the context of this application the known "cold gas spraying method" (cold spray-

ing) is also understood to be covered by the term "thermal spraying method" in addition to all known spraying methods.

In this connection thermal spraying has opened up large areas of use. One can certainly state that thermal spraying as a surface coating technique is the coating technique which probably has the largest scope of use. A delimitation of the areas of use of the spraying methods listed above does not appear necessarily sensible in this connection because the areas of use can overlap with each other.

It was a great problem for a long time in this connection to provide large surface areas in sufficient uniformity, in particular with thin layers with thickness in the micrometer range by means of thermal spraying methods. The low pressure thermal method ("LPPS method") suggested in EP 0776 594 B1 from Sulzer Metco has brought about a breakthrough here, which, using a broad/wide plasma beam, allows the manufacture of uniform coatings on large surfaces, on metal sheets for example. On the one hand this is achieved by means of the geometric design of the spray gun, with it moreover being important that a substantial pressure difference prevails between the inside and the outside of the spray gun. The workpiece, or at least the surface area of the workpiece, which is to be coated, is located in a coating chamber in this arrangement, in which, in relation to the inside of the spray gun, a sub-atmospheric pressure is produced, for example a sub-atmospheric pressure of less than 100 mbar, while in the spray gun a pressure of approximately 1000 mbar prevails, in other words approximately ambient pressure. A broad coating beam can be produced by setting a pressure gradient of this kind between the inside of the spray gun and the coating chamber, with which the surface of the workpiece can be coated with a uniformity never previously attainable.

In this connection this basic principle has in the meantime been developed considerably further. EP 1 479 788 A1 shows for example a hybrid method which builds on the basic method of EP 0776 594 B1.

In this connection these methods are particularly suitable to apply different metallic or non-metallic coatings, in particular also ceramic, carbidic or nitridic layer components in thin layers.

Modern technical demands however are moving toward the replacement of even the multi-stage galvanic or electrolytic method described above with reference to an exemplary process by thermal spraying methods, since the thermally sprayed layers can be applied principally in one method step and much more efficiently, in other words with clearly higher deposition rates, i.e. in a much shorter time.

In this connection one has hitherto been of the opinion that the classical thermal spraying method, in particular the LPPS method outlined briefly above and also the cold gas spraying method, are fundamentally not suitable for coating with zinc and zinc compounds. The reason for this prejudice is that zinc has an enormously high vapour pressure even at relatively low temperatures. Thus zinc for example already has a vapour pressure of approximately 1000 mbar at approximately 900° C, while aluminium only reaches roughly the same vapour pressure at approximately 2000° C and Al_2O_3 only displays it at about 3000° C.

Thus one has assumed up to now that the LPPS method is not worth considering for the thermal spraying of zinc-containing layers primarily, but not only, because it was presumed that due to its high vapour pressure the zinc already escapes in the coating beam to such a large extent that no useful zinc-containing layers can be manufactured by means of ther-

mal spraying. In this connection not only is the high vapour pressure of the zinc as such is regarded as a fundamental problem, but also the large difference in the vapour pressure from other materials, which can be sprayed at the same time as the zinc. If namely, a different material is sprayed simultaneously together with zinc, which is for example separately sprayed simultaneously with zinc, but at a considerably lower vapour pressure, then it has to be feared that already the ratio of the composition of zinc to further spraying materials will alter massively in the coating beam, so that the sprayed layers no longer have the desired composition and thus the necessary corrosion protection cannot be attained.

Accordingly, no suitable zinc-containing spray materials and consequently also no corresponding thermal spraying methods exist in the prior art.

Thus the object of the invention is to make available a thermal spraying method, so that thermally sprayed surfaces can be manufactured by means of a thermal spraying method, which offer at least a corrosion protection which is at least equally good in comparison with the conventional layers, for example galvanically applied layers. Furthermore, it is an object of the invention to make available a thermal spraying method using which a corresponding surface layer can be manufactured.

The subjects of the invention, which satisfy these objects from a method and apparatus point of view are characterised by the features of the independent claims in the respective category.

The respective dependent claims relate to particularly advantageous embodiments of the invention.

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The invention thus relates to a thermal spraying material for the coating of a surface of a workpiece by means of a thermal spraying method, wherein the spraying material contains zinc.

Thus, it is fundamental to the spraying material in accordance with the invention that it
5 contains zinc. The presence of zinc in a coating sprayed with the spraying material guarantees namely, possibly with the addition of further suitable elements, that the workpiece provided with the zinc coating, for example a sheet made of steel, aluminium or another suitable metal or a suitable metal alloy, is optimally protected against corrosion. The fact that the spraying material in accordance with the invention can be used at all for a thermal spraying method is
10 due to the recognition that by a suitable selection of the coating parameters, which is described in more detail below, the spraying of materials with high vapour pressure, is possible, even in combination with other materials which have a considerably lower vapour pressure.

According to one aspect of the present invention, there is provided a thermal spraying powder
15 for coating of a surface of a workpiece by means of a thermal spraying method, wherein the spraying powder consists of one of a zinc alloy, an intermetallic compound, a metallic compound or a non-metallic compound, and is of the kind Zn-X, wherein Zn is contained in the range of 70% by weight to less than 100% by weight, and X consists of one or more members selected from the group consisting of Sn, Mg, Ca, Fe, Ni, Co, Cu, Mo, Ti, Cr, Zr, Y,
20 La, Ce, Sc, Pr, Dy, C, O, N, and compounds and combinations thereof, wherein a first one of the selected members is Sn in the amount of 1% to 4% by weight of the spraying powder.

In a preferred embodiment the spraying material is a zinc alloy and/or a intermeteallic compound and/or a metallic compound and/or a non metallic compound of the kind Zn-X, wherein X is at least a metallic or a non-metallic component, Zn is contained in the range of
25 70% by weight to 100% by weight, preferably with more than 80% by weight, and wherein X is at least one element from the group comprising of the elements Sn, Mg, Ca, Al, Fe, Ni, Co, Cu, Mo, Ti, Cr, Zr, Y, La, Ce, Sc, Pr, Dy, Dg, C, O, N in particular a MCrAlY alloy, wherein M=Ni, Co, CoNi or Fe.

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The combinations of the elements Cu, Ni, Co, Mo, play a special role in this, which among other things, but not just, have an influence on the toughness of the layer to be sprayed.

In an embodiment which is particularly important for practical use tin (Sn) is contained in the spray powder as an alloying element with a proportion of up to 10% by weight, in particular up to 5% by weight, especially between 1% and 4% by weight. Among other things a strengthened bond between the zinc (Zn) particles can be attained during the diffusion by the addition of Sn. An eutectic for example, with a melting point of approximately 200° C can be formed about the Sn particles, which can considerably accelerate the diffusion during the heat treatment. This point will be explained again later in context in the description of the method in accordance with the invention. In order to achieve the described effect, it is particularly advantageous when the starting material Zn is already alloyed prior to the spraying, in other words is alloyed with Sn in the spray powder itself.

In another embodiment the spraying material can include a Mg-Zn alloy, in particular MgZn_2 and/or a ZnAl_a alloy, in particular with $1\% \leq a \leq 10\%$ by weight, especially with $4\% \leq a \leq 6\%$. In this connection the alloying with Al leads on the one hand to the melting point of the alloy being reduced and to the vapour pressure of pure zinc being simultaneously reduced.

In particular, for the increase of the hardness and/or of the wear protection characteristics of a coating which is to be sprayed, but not only for this purpose, a spraying material in accordance with the invention can include an oxidic component and/or a ceramic component, in particular MgO and/or Al_2O_3 and/or a carbide, in particular SiC and/or a nitride, in particular AlN and/or can contain a compound of the type $\text{M}_x\text{O}_y\text{N}_z$, wherein M is a metal, in particular Zr, Al, Cr, Ti, Ta or another material which forms a thermodynamically stable compound of this type. In this

connection the resistance to scratches of the surface is in particular increased by the addition of the hard ceramic materials.

In this connection the possible additional components in the spraying material are of course dependent on the application in which a workpiece to be coated is to be employed. The spraying material is preferably no longer an homogenous alloy but rather a compound material, for example a finely agglomerated material with a particle diameter from the nanometer range up to and into the micrometer range.

Furthermore, the invention relates to a thermally sprayed coating on a surface of a workpiece, wherein the surface layer contains zinc.

In this connection the coating can include pure zinc, a zinc alloy and/or an intermetallic compound and/or a non metallic composite of the kind Zn-X, wherein X is at least a metallic or a non-metallic component, Zn is contained in the range of 70% by weight to 100% by weight, preferably with more than 80% by weight, and wherein X is at least one element from the group comprising of the elements Sn, Mg, Ca, Al, Fe, Ni, Co, Cu, Mo, Ti, Cr, Zr, Y, La, Ce, Sc, Pr, Dy, Dg, C, O, N in particular a MCrAlY alloy, wherein M is equal to Ni, Co, CoNi or Fe.

In an embodiment which is particularly important for practical use, the thermally sprayed coating contains tin (Sn) with a proportion of up to 10% by weight, in particular up to 5% by weight, especially between 1% and 4% by weight as an alloying element in the surface layer. As has already been mentioned, a strengthened connection between the zinc (Zn) particles can be attained in the diffusion process by the addition of Sn. For example, a eutectic with a melting point of approximately 200° C can namely form about the Sn particles, which can considerably accelerate the diffu-

sion during a heat treatment which is possibly carried out after the application of the coating. In order to achieve the described effect it is particularly advantageous if the starting material Zn is already alloyed with Sn prior to spraying, in other words is already alloyed with Sn in the spray powder itself.

In another embodiment of a thermally sprayed coating in accordance with the invention the coating includes a Mg-Zn alloy, in particular MgZn_2 and/or a ZnAl_a alloy, in particular with $1\% \leq a \leq 10\%$ by weight, especially with $4\% \leq a \leq 6\%$, and/or the coating contains an oxidic component and/or a ceramic component, in particular MgO and/or Al_2O_3 and or a carbide, in particular SiC and/or a nitride, in particular AlN. In this connection the alloying of Al leads, on the one hand, as already mentioned, to the melting point of the alloy being reduced and simultaneously to the vapour pressure of pure zinc being reduced.

The coatings with oxidic and/or carbidic and/or ceramic components are distinguished in particular by a high degree of hardness and/or a good resistance to wear. In the case of these hard layers containing for example SiC or AlN, or other components of these material classes, the addition or doping with relatively small amounts can have a considerable influence on the corresponding characteristics. By this means the cohesion between the particles is improved in particular and /or the columnar construction of the crystal structure in the coating is assisted.

In another example, the spraying material contains a compound of the type $\text{M}_x\text{O}_y\text{N}_z$, wherein M is a metal, in particular Zr, Al, Cr, Ti, Ta or another material, which forms a thermodynamically stable compound of this type.

The thickness of the coating is preferably between $1\mu\text{m}$ and $100\mu\text{m}$, in particular between $2\mu\text{m}$ and $50\mu\text{m}$, especially between $2\mu\text{m}$ and $20\mu\text{m}$ which is particularly advantageous for large metal sheets, such as are used in the automotive field, but not only there.

The invention further relates to a thermal spraying method for the formation of an above-described coating on a surface of a workpiece, wherein a spray material containing zinc in accordance with the present invention is used.

In this connection a workpiece to be coated is introduced into a process chamber or into a coating chamber and a gas atmosphere is adjusted to a predetermined gas pressure in the process chamber and the workpiece is coated with a coating beam at the predetermined gas pressure.

In this connection a gas pressure of less than 100 mbar is preferably set in the process chamber, preferably a gas pressure between 1 mbar and 10 mbar, especially between 1 mbar and 2 mbar and/or a medium spraying distance between 800 mm and 30000 mm, in particular between 1000 mm and 2000 mm, especially between 1000 mm and 1400 mm.

In an embodiment, which is particularly important for practical use of a method in accordance with the invention, a pressure ratio of 1 to 40, in particular of between 5 and 30, especially a pressure ratio of approximately 10 to 20 is set between a pressure in the interior of the coating beam and the gas pressure of the gas atmosphere. In other words a gas pressure of the gas atmosphere is preferably selected which is less than the pressure in the interior of the coating beam, for example in a plasma beam at the outlet of the spray gun. This selection of the pressure parameters is also termed an "under-expanded condition". The selection of

these parameters is in particular very advantageous when the spray material contains a material, which vaporises easily, in other words has a high vapour pressure for example.

It has been shown, namely, that shock-like waves or conditions form in a coating beam which for example diverges supersonically, which form a barrier for the material located in the coating beam, so that essentially it can not escape from the coating beam. This means that the beam functions in the same way as a light conductor for light, as a totally reflecting barrier, so that the vaporised material is trapped in the coating beam and thus materials with a high vapour pressure can also be sprayed. This effect is aided by the fact that a quasi laminar flow is present in the marginal zone of a thermal coating beam, i.e. that the turbulence is greatly reduced in this marginal zone.

In this connection a pressure gradient of 0.001 mbar/mm to 0.02 mbar/mm, in particular from 0.0005 mbar/mm to 0.01 mbar/mm, is particularly advantageously set, seen along the length of the coating beam.

It is to be understood that not only solid, liquid and gaseous, in other words vaporised components can be contained in the coating beam. A combination of liquid components and gaseous components in particular leads to particularly advantageous coatings. For the deposition of vaporised materials it is particularly important that a clean surface of the workpiece is available. Hot, substantially liquid zinc droplets on the surface of an oxide-containing substrate can react with the oxide and then adhere very well, so that essentially liquid droplets, particularly of zinc, are very advantageous for the adhesion of the coating which is to be built up, at least for the formation of the parts of coating which is in direct contact with the surface of the substrate.

The temperature of the workpiece is advantageously adjusted to a predetermined value during coating, in particular to a temperature between room temperature and 550° C, especially to a temperature between room temperature and 400° C.

After coating the coated workpiece can, if necessary, be further heat treated at a predetermined temperature, in particular at a temperature between 400° C and 650° C, especially at approximately 550° C. In this connection the heat treatment can, among other things, lead to a homogenising and/or densification of the sprayed-on coatings, can improve the bonding of the coating to the substrate, can decrease the surface roughness and/or lead to the formation of preferred oxides or metallic and/or non-metallic compounds, which can positively influence the corrosion resistance, the resistance to wear or other physical or chemical characteristics or the coating, among other things.

In special cases it is also possible that additional protecting cover layers, in particular also organic cover layers are applied, in particular with LPPs hybrid processes such as are described in EP 1 479 788 A1, so that for example coatings with optimal corrosion protection are produced on a workpiece.

Due to the fact that all process steps are preferably carried out simultaneously or one after the other in the process chamber, no oxidic contaminants arise which facilitates a simple carrying out of the process and leads to a better diffusion, both in and between the particles and also between adjacent layers. Very high surface regions which are obtained when thin layers are built up by more or less liquid droplets, lead to lower sintering temperatures during the heat treatment and thus to thicker coatings.

Depending on the requirements it can be advantageous in this connection, to undertake cleaning of the surface from organic and/or oxidic contaminants, before and/or during the coating process, preferably by means of arc cleaning or ablating.

It goes without saying that multi-layer systems, which are composed of individual layers of the same or different chemical and/or structural composition can naturally likewise also be applied to a workpiece, using a method in accordance with the invention. It goes without saying, that gradient layers can also be produced, e.g. by altering method parameters during a coating process in a controlled fashion and/or by altering the composition of the spraying material.

Fundamentally, all thermal spraying methods known per se can be advantageously used for the carrying out of a method in accordance with the invention, i.e. the spraying method is a plasma spraying method, in particular a LPPS method, especially a LPPS thin film method, an HVOF method, a cold gas spraying method, a flame spraying method, especially a wire spraying or powder spraying method or another thermal spraying method, if only the parameters and spraying conditions are selected in accordance with the present invention.

As has already been mentioned several times, the invention further relates to the use of a material in accordance with the invention for the coating of a surface of a workpiece by means of a thermal spraying method.

Furthermore, the invention also relates to a workpiece, in particular to a large metal sheet, especially to a metal sheet made of aluminium and/or to iron and/or steel and/or to a metal and/or to a metal alloy and /or to

another material, onto which a coating in accordance with the present invention is applied with a material in accordance with the invention. It is to be understood that a workpiece in accordance with the invention can naturally also be coated on both sides.

An important effect of a special embodiment of a method in accordance with the invention will be explained more closely in the following with the help of the drawings, which show:

Fig. 1 an under-expanded/over-expanded pressure diagram;

Fig.2 the effect of the under-expanded condition on the flow of particles in the coating beam.

A diagram is illustrated in Fig. 1 in which pressure values are recorded on the ordinate, such as for example could arise during plasma spraying at the outlet 4 of a nozzle 3 of a spray gun 2, and, on the abscissa, gas pressures such as, for example could be set in a process chamber during the coating of a substrate. In this connection, the separating line 1 separates the diagram into two part regions, which are characterised with "under-expanded" and "over-expanded". In the under-expanded region, the pressure at the outlet 4 of the nozzle 3 is higher than the gas pressure in the process chamber. On the other hand, in the over-expanded part region, the gas pressure in the process chamber is higher than the pressure at the outlet 4 of the nozzle 3.

In carrying out of a method in accordance with the invention the pressure parameters are preferably selected so that coating takes place in the under-expanded region.

Fig. 2 shows in a schematic manner how the selection of the pressure parameters in the under-expanded region affects the movement of a spraying material 5 in a coating beam 6.

In Fig. 2 a section of a plasma spray gun 2 is schematically illustrated from which a coating beam 6 discharges from a nozzle 3. The coating beam 6 is ultrasonic so that shock waves form in the coating beam 6. The formation of the shock waves is illustrated symbolically by the wavelike outline of the coating beam 6. On the right hand side in Fig. 2 there is a not-illustrated substrate, which is coated by the coating beam 6.

In the example of Fig. 2 a gas pressure of the gas atmosphere in the process chamber is selected, which is smaller than the pressure at the outlet 4 of the spray gun 2. This selection of the pressure parameters corresponds to the part region "under-expanded" in the diagram of Fig. 1. The selection of these parameters is, as has already been mentioned, particularly advantageous when the spray material 5 contains a material, which vaporises easily, in other words has a high vaporising pressure.

The coating beam 6 of Fig. 2 spreads ultrasonically, so that shock-like waves or conditions form which represent a barrier for the material 5 located in the coating beam 6, so that this essentially can not leave the coating beam 6. This means that the coating beam 6 has a similar effect to a light conductor for light, as a more or less totally reflecting barrier, so that the vaporised material is caught in the coating beam and, for example, follows the path 7 in the direction towards the substrate to be coated. For this reason it is possible to also coat materials with high vapour pressure, such as for example with Zn, using a method in accordance with the present invention.

In this connection it goes without saying that the invention is not limited to the described embodiments and, in particular, the embodiments in accordance with the invention described within the context of this application can, of course, also be combined in any suitable manner.

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CLAIMS:

1. A thermal spraying powder for coating of a surface of a workpiece by means of a thermal spraying method, wherein the spraying powder consists of one of a zinc alloy, an intermetallic compound, a metallic compound or a non-metallic compound, and is of the kind
5 Zn-X, wherein Zn is contained in the range of 70% by weight to less than 100% by weight, and X consists of one or more members selected from the group consisting of Sn, Mg, Ca, Fe, Ni, Co, Cu, Mo, Ti, Cr, Zr, Y, La, Ce, Sc, Pr, Dy, C, O, N, and compounds and combinations thereof, wherein a first one of the selected members is Sn in the amount of 1% to 4% by weight of the spraying powder.
- 10 2. A thermal spraying powder in accordance with claim 1, wherein X consists of two or more members selected from the group consisting of Sn, Mg, Ca, Fe, Ni, Co, Cu, Mo, Ti, Cr, Zr, Y, La, Ce, Sc, Pr, Dy, C, O, N, and compounds and combinations thereof;
wherein the first one of the selected members is the Sn in the amount of 1% to 4% by weight of the spraying powder; and
15 wherein a second one of the selected members is Mg, and the spraying powder is a Mg-Zn alloy.
3. A thermal spraying powder in accordance with claim 2, wherein the Mg-Zn alloy comprises an MgZn₂ alloy.
4. A thermal spraying powder in accordance with claim 1, wherein X consists of
20 two or more members selected from the group consisting of Sn, Mg, Ca, Fe, Ni, Co, Cu, Mo, Ti, Cr, Zr, Y, La, Ce, Sc, Pr, Dy, C, O, N, and compounds and combinations thereof;
wherein the first one of the selected members is the Sn in the amount of 1% to 4% by weight of the spraying powder; and
wherein a second one of the selected members consists of at least one of an
25 oxidic component, a ceramic component, or a compound of the type M_aO_bN_c, wherein M is

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selected from the group consisting of Sn, Mg, Ca, Fe, Ni, Co, Cu, Mo, Ti, Cr, Zr, Y, La, Ce, Sc, Pr, Dy, and C, wherein a, b, and c are positive integers.

5. A thermal spraying powder according to claim 4, wherein the at least one of the oxidic component and the ceramic component comprises at least one of the MgO or
5 carbide.
6. A thermal spraying powder in accordance with claim 5, wherein the at least one of the oxidic component or the ceramic component further comprises a nitride.
7. A thermal spraying powder in accordance with claim 4, wherein the second one of the selected members consists of a ceramic component.
- 10 8. A thermal spraying powder in accordance with claim 4, wherein the second one of the selected members consists of the compound of the type $M_aO_bN_c$, wherein M is selected from the group consisting of Sn, Mg, Ca, Fe, Ni, Co, Cu, Mo, Ti, Cr, Zr, Y, La, Ce, Sc, Pr, Dy, and C, wherein a, b, and c are positive integers.
9. A thermal spraying powder in accordance with claim 8, wherein the compound
15 of the type $M_aO_bN_c$ is a thermodynamically stable compound.
10. A thermal spraying powder in accordance with claim 9, wherein M consists of Zr, Cr, Ti, or combinations or compounds thereof.
11. A thermal spraying powder in accordance with claim 1, wherein X consists of the Sn in the amount of 1% to 4% by weight of the spraying powder, and at least one member
20 selected from the group consisting of Fe, Co, Cu, Mo, Ti, Zr, Y, La, Ce, Sc, Pr, Dy, C, O, N, and compounds and combinations thereof.
12. A thermally sprayed coating on a surface of a workpiece comprising a thermal spraying powder as defined in any one of claims 1 to 11.
13. A thermally sprayed coating in accordance with claim 12, wherein the coating
25 has a thickness of between 1 μm and 100 μm .

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14. A thermally sprayed coating in accordance with claim 12, wherein the coating has a thickness of between 2 μm and 50 μm .

15. A thermally sprayed coating in accordance with claim 12, wherein the coating has a thickness of between 2 μm and 20 μm .

5 16. A thermal spraying method for formation of a thermal sprayed coating as defined in any one of claims 12 to 15 on a surface of a workpiece, wherein a thermal spraying powder as defined in any one of claims 1 to 11 is applied to the surface of the workpiece.

10 17. A thermal spraying method in accordance with claim 16, wherein a coated workpiece is brought into a process chamber and a gas atmosphere in the chamber is adjusted to a gas pressure and the workpiece is coated with a beam comprising the thermal spraying powder.

18. A thermal spraying method in accordance with claim 17, wherein the gas pressure in the process chamber is less than 100 mbar.

15 19. A thermal spraying method in accordance with claim 17, wherein the gas pressure in the process chamber is between 1 mbar and 10 mbar.

20. A thermal spraying method in accordance with claim 17, wherein the gas pressure in the process chamber is between 1 mbar and 2 mbar.

20 21. A thermal spraying method in accordance with any one of claims 17 to 20, wherein the powder is applied to the surface of the workpiece from a distance of between 400 mm and 3000 mm.

22. A thermal spraying method in accordance with any one of claims 17 to 20, wherein the powder is applied to the surface of the workpiece from a distance of between 800 mm and 2000 mm.

25 23. A thermal spraying method in accordance with any one of claims 17 to 20, wherein the powder is applied to the surface of the workpiece from a distance of between 1000 mm and 1400 mm.

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24. A thermal spraying method in accordance with any one of claims 17 to 23, wherein a pressure ratio is set between a pressure in the interior of the coating beam and the gas pressure of the gas atmosphere, and the pressure ratio is from 1 to 40.
25. A thermal spraying method in accordance with any one of claims 17 to 23,
5 wherein a pressure ratio is set between a pressure in the interior of the coating beam and the gas pressure of the gas atmosphere, and the pressure ratio is from 5 to 30.
26. A thermal spraying method in accordance with any one of claims 17 to 23, wherein a pressure ratio is set between a pressure in the interior of the coating beam and the gas pressure of the gas atmosphere, and the pressure ratio is from 10 to 20.
- 10 27. A thermal spraying method in accordance with any one of claims 17 to 26, wherein a pressure gradient is set over the length of the coating beam of 0.001 mbar/mm to 0.02 mbar/mm.
28. A thermal spraying method in accordance with any one of claims 17 to 26,
15 wherein a pressure gradient is set over the length of the coating beam of 0.005 mbar/mm to 0.01 mbar/mm.
29. A thermal spraying method in accordance with any one of claims 17 to 28, wherein workpiece is set at a temperature between room temperature and 550°C during the coating.
30. A thermal spraying method in accordance with any one of claims 17 to 28,
20 wherein workpiece is set at a temperature between room temperature and 400°C during the coating.
31. A thermal spraying method according to any one of claims 17 to 30, wherein the workpiece is heat treated after the coating at a temperature between 400°C and 650°C.
32. A thermal spraying method according to any one of claims 17 to 30, wherein
25 the workpiece is heat treated after the coating at a temperature of approximately 550°C.

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33. A thermal spraying method in accordance with any one of claims 16 to 32, wherein the spraying method is a plasma spraying method, an HVOF method, a cold gas spraying method, a flame spraying method, or a powder spraying method.
34. A thermal spraying method in accordance with claim 33, wherein the plasma
5 spraying method is a CPPS method.
35. A thermal spraying method in accordance with claim 34, wherein the CPPS method is an CPPS thin film method.
36. A thermal spraying method in accordance with claim 33, wherein the flame spraying method is a wire flame spraying method.
- 10 37. A use of a thermal spraying powder as defined in any one of claims 1 to 11 for coating of a surface of a workpiece by means of a thermal spraying method, as defined in any one of claims 16 to 36.
38. A workpiece coated with a thermally sprayed coating as defined in any one of claims 12 to 15.
- 15 39. A workpiece in accordance with claim 38, wherein the workpiece is a sheet of metal coated with the thermally sprayed coating.
40. A workpiece in accordance with claim 39, wherein the metal is one or more of aluminium, iron and steel or is a metal alloy.

Fig.1

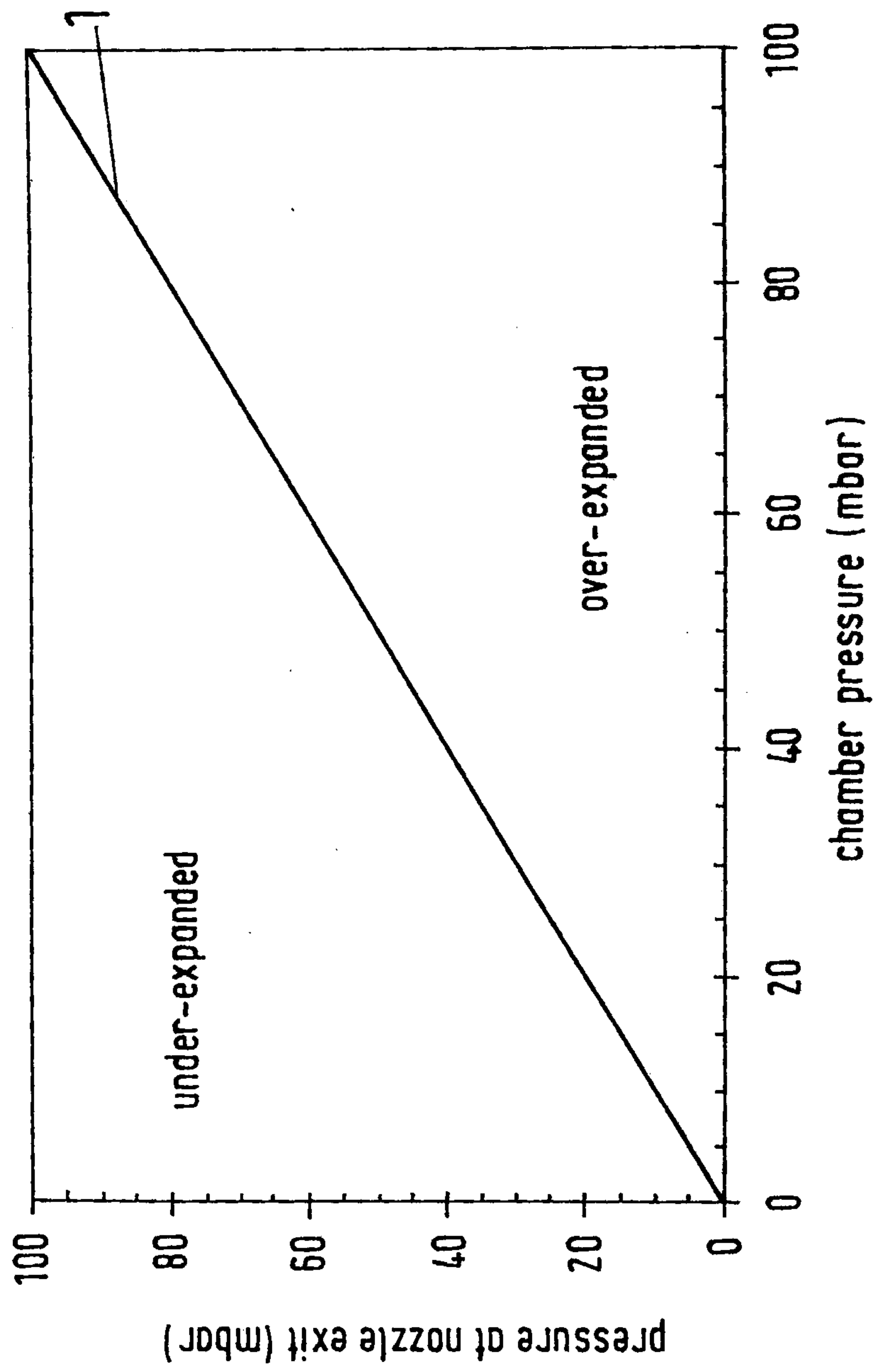


Fig.2

