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Method for the production of a ceramic layer on a metallic base material

The invention relates to a method for the production of a ceramic layer on a metallic base material, to an apparatus for carrying out the method and to workpieces manufactured in accordance with the method. The method in accordance with the invention can be used for example as a surface technology in turbine wheels (for the protection of the blades or blade tips in gas and steam turbines or in Pelton wheels) or in diesel engines (pistons, cylinder heads, valves).

Metallic surfaces can in principle be substantially improved with respect to various properties by means of ceramic coatings, namely for example with respect to their resistance to wear and/or to corrosion. The coating can also be used at higher temperatures as a heat insulating layer and as protection against wear. Pairing a ceramic material with a metallic one is very difficult due to the great differences between these materials. It is an object of the invention to apply a technically usable ceramic layer to a metallic base material by means of a suitable method and with a suitable choice of materials. Claim 1 summarises the features by means of which this object is satisfied in accordance with the invention.

The method for the manufacture of a ceramic layer on a metallic base material combines the following measures: The base material is preheated. Ceramic coating material is applied to a locally melted surface region of the base material. In this situation the coating material is likewise melted. A metallurgical bonding zone is produced by means of an additional material which reacts with the coating material and which is additionally applied to the base material as an adhesion producing layer or is admixed with the base material as a component of the alloy.

Thanks to the bonding zone in accordance with the invention the layer adheres well to the base material. Materials must be selected for which a bonding zone or an intermediate layer of this kind forms. In the choice of the materials care must further be taken that the ceramic layer has a suitable microstructure and that only low residual tensions remain between the layer and the base material. In particular the production of a layer should be possible which is intact, i.e. largely free of tears, and compact, i.e. largely free of pores. For special applications porous coatings can also be advantageous. The method in accordance with the invention enables the manufacture of ceramic coatings of which the layer thicknesses are at least 0.1 mm, with it being possible for the layer thicknesses to be considerably greater.

The energy which is required for the melting of the ceramic coating material and for the piece of surface of the base material to be melted is advantageously introduced by means of a laser beam. Ceramic materials are very good absorbers in the infrared range so that a coating material present in powder form is preheated when flying through the laser beam.

The base material, including the adhesion producing layer where appropriate, forms the substrate. The laser is directed at this substrate. The powder particles which fly through the laser beam and are thereby preheated encounter a melt puddle formed by the laser beam in an interaction zone on the substrate. In the presence of an adhesion producing layer the additional material at the surface of the substrate is transported in the interaction zone through convection and diffusion partially into the base material and partially into the coating material, where it forms transition regions as a result of metallurgical reactions which mechanically stably bond the base material to the ceramic coating after the subsequent solidification of the melt puddle.

The base material is advantageously a ferrite steel with low carbon content. A Martensite formation is largely absent during the cooling of a steel of this kind.

A specific coating method will be explained in the following:

A mixture of Al_2O_3 and ZrO_2 is used as a coating material, advantageously in a relationship of the two oxides for which a eutectic results (42 % ZrO_2 by weight) so that the melting point of the layer takes on a minimum value (about 1900°C). This mixture has a relatively large coefficient of thermal expansion for ceramic materials, namely about $8 \cdot 10^{-6} \text{ K}^{-1}$. A steel is used as a base material, the coefficient of thermal expansion of which is relatively small in comparison with other metals, namely a superferritic steel (X1 CrNiMo, coefficient of thermal expansion: $10.5 \cdot 10^{-6} \text{ K}^{-1}$, melting point 1485°C ; composition in percent by weight: 0.003 C, 28.35 Cr, 3.35 Ni, 2.37 Mo, 0.38 Si, 0.37 Mn, remainder Fe). It is important that the

coefficient of thermal expansion of the superferritic steel is somewhat greater than that of the ceramic layer in order that the coating is under a compression force after the cooling down. Titanium (Ti) is chosen for the adhesion producing layer.

Titanium as an adhesion producing layer can be applied to the base material by means of PVD (Physical Vapour Deposition). The application of the coating must be carried out screened off from oxygen and nitrogen, i.e. in a protective gas (Ar).

When the substrate melts, Ti diffuses out of the adhesion producing layer into the base material and into the oxide incident at the interaction zone. Oxygen proceeds from the oxide into the melted adhesion producing layer and oxidises Ti there, whereas zirconium oxide (ZrO_2) is partially reduced in a boundary region of the ceramic coating material. Assimilations of the chemical compositions thereby result in a transition region between the substrate and the coating. This transition region forms a mechanically stable bonding zone.

In the adhesion producing layer the Ti can be partially or wholly replaced by Zr or Hf. Other alloys also come into consideration as base materials which have relatively low coefficients of thermal expansions and melting points which do not differ greatly from those of the ceramic layer. One can for example use a ferritic construction steel. In this case the adhesion producing layer must be relatively thick (several hundredths of a millimetre) so that a volume increase through Martensite-wise conversions acts to a reduced extent on the ceramic layer. MeCrAlY (with Me = Fe, Ni, Co) can be used as a material for the adhesion producing layer which can be applied by means of laser

coating. It is ideal if the values for the coefficients of thermal expansion and the melting temperatures are located between the corresponding values for the base material and the ceramic coating in the bonding zone.

For a successful production of a coating which adheres to the base material in accordance with the invention as a result of a bonding zone it is necessary in addition that the substrate be preheated. The heat required for the preheating is advantageously introduced inductively by means of electromagnetic energy. Preheating is done to a temperature T_a , with the absolute temperature T_a being greater than about 50% of the melting temperature T_m of the base material.

The coating manufactured in accordance with the invention is also resistant to thermal shock. Relatively large temperature gradients between the coating and the base material are possible without a breaking off of the ceramic layer arising.

The invention will be explained in more detail in the following with reference to the drawings. Shown are:

- Fig. 1 a schematic illustration of a first apparatus for the manufacture of the coating in accordance with the invention,
- Fig. 2 a part of a second apparatus, namely a nozzle for supplying a protective gas into which a second nozzle for a powder injection is integrated,
- Fig. 3 a second exemplary embodiment of the protective gas nozzle.

The apparatus in Fig. 1 comprises the following components: a workpiece 1 to be coated, a laser system 2, a powder dispenser 3 (reservoir inclusive of forwarder), an energy source 4 for an induction heater, an apparatus 5 for moving the workpiece 1, a tightly closing container 6 and a reservoir 7 for a protective or inert gas. Coating material in powder form is applied via a hose 32 and a nozzle 31 to an interaction zone 10 on the workpiece 1 under the action of a laser beam 20. At the same time heat is produced inductively in the workpiece 1 by means of an electrode 40 which is connected to an energy source 4 via electrical lines 41a and 41b. The workpiece 1 is moved by the apparatus 5 at an advancing speed v in the x direction so that a uniform trail 12 of applied material 30 arises. Through displacement of the workpiece 1 in the y direction an array of further trails can be manufactured in parallel and close arrangement. The electrode 40 of the induction heater can be arranged to be fixed in space depending on the size of the workpiece 1; it can however also be moved along with the workpiece 1. The container 6, in which the coating is carried out in a protective gas atmosphere, is connected to the gas reservoir 7 via a line 71. A window 21 in the wall of the container 6 allows the (infrared) laser beam to pass.

A control apparatus (not shown) can also be provided by means of which process parameters, in particular the advancing speed of the movable holder 5, can be regulated as a result of temperature measurements at and on the workpiece 1. The cooling down of the base material can be controlled using the control apparatus in such a manner that the cooling down speeds of the base material and of the coating are of the same order of magnitude, i.e. do not differ by more than a factor of five.

Instead of in the protective gas atmosphere of the container 6, it is advantageous to carry out the method in accordance with the invention by means of a suitably formed protective gas nozzle 60 — see Fig. 2: a large nozzle 60 for the supply of the protective gas 77 within which space is provided for the laser beam 20, and a small nozzle 31, with coating material 33 consisting of powder particles 30 being supplied using the small nozzle 31. The protective gas 77 is guided in the form of a laminar flow to the nozzle opening 61 in a ring gap between the wall of the large nozzle 60 and a tube piece 22 from which the laser beam 20 emerges. After it emerges from the nozzle opening 61 the protective gas 77 — flowing further in a laminar manner — forms a barrier 70 against the surrounding air space. This barrier 70 is dimensioned in such a manner that a diffusing in of the surrounding air to the interaction zone 10 is suppressed. The parts of the apparatus which are located in the protective gas flow are suitably formed so that a laminar development of the flow of the protective gas 77 is ensured; in particular the powder nozzle 31 is formed in a streamlined shape.

The workpiece 1 is coated with an adhesion producing layer 11 of a material with which a bonding zone 12' can be produced in accordance with the invention. In the melting puddle of the interaction zone 10 this material distributes itself in a region 11' indicated by dots; in this situation it combines on the one hand with the base material 1' and, on the other hand, with the incident coating material 30. Through the application of material onto the workpiece 1, which is moved at a speed v , a trail 12 arises which together with further trails applied parallel to it forms a connected coating material 30.

Fig. 3 shows a protective gas nozzle 60 with the following components: a flange 23, an intermediate ring 24, ZnSe windows 21 (transparent for infrared), protective gas connections 72, a ring passage 61, a gap-shaped passage aperture 62 and a powder nozzle 30 with a connection hose 31. In this example the focus 25 of the laser beam 20 is located above the interaction zone 10 of the workpiece 1. The protective gas 77 is fed into the inner space of the nozzle 60 via the gap 62 in such a manner that a uniform laminar flow develops.

For the production in accordance with the invention of a bonding zone 12' it is not necessary that the additional material which is required for this, for example Ti, is applied in the form of an adhesion producing layer 11 (see Fig. 2) which must be manufactured with the ceramic material 30 in a separate step prior to the coating. It is also possible to introduce the additional material into the interaction zone 10 for example together with the ceramic material or by means of a second powder nozzle (not shown) immediately prior to the application of the ceramic material 30. A further possibility consists in adding the additional material during the casting of the base material for the manufacture of a cast part. The additional material can also be a constituent of an intermediate layer.

Particles can also be added to the ceramic coating material 30 which are chemically largely stable with respect to liquid melt phases arising in the coating procedure. These particles can consist of hard ceramic materials such as carbides, nitrides, borides and/or oxides or can be enveloped in resistant protective coatings. Particles of this kind can serve for the improvement of the wear resistance. The particles are admixed to the powder of the coating material; they can however also be introduced into

the laser induced melt puddle by a separate powder supply.

The method in accordance with the invention can be used to manufacture coatings for protection against thermo-mechanical or chemically corrosive stressing, for example for the protection of turbine wheels. Heat insulation at higher temperatures and wear protection are further possible uses.

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Patent Claims

1. Method for the manufacture of a ceramic layer (12, 13) on a metallic base material (1'), wherein the base material is held at an elevated temperature, ceramic coating material (30) is applied to a locally melted surface region (10) of the base material and is likewise melted so that a metallurgical bonding zone (12') forms with an additive material, with the additive material, which is additionally applied to the base material as an adhesion promoting layer (11), or is added to the base material as a component of the alloy, reacting with the coating material.
2. Method in accordance with claim 1, characterised in that the base material (1') is preheated to a temperature T_G , with electromagnetic energy in particular being advantageously introduced inductively and the absolute temperature T_G being greater than about 50% of the melting temperature T_m of the base material.
3. Method in accordance with claim 1 or claim 2 characterised in that the coating material (30) and the surface to be coated are melted at the same time by means of a laser beam (20), with the laser beam being directed toward the place to be coated and with the coating material being forwarded through the beam in powder form.
4. Method in accordance with one of the claims 1 to 3 characterised in that material (11) additionally



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applied to the base material (1') for the production of the bonding zone (12') is applied by means of a separate method step, in particular by a laser coating, by an application from the vapour phase (PVD) or by thermal spraying.

5. Method in accordance with one of the claims 1 to 4 characterised in that the application of material is performed in a laminarly flowing protective gas (70), with a diffusion of air from the surroundings to the places (10) to be coated being largely suppressed by means of the gas flow.
6. Method in accordance with one of the claims 1 to 5 characterised in that the cooling down of the base material is controlled by means of a control apparatus in such a manner that the cooling rates of the base material and of the layer are of the same order of magnitude, i.e. do not differ by more than a factor of five.
7. Apparatus for the coating of a workpiece (1) by means of the method in accordance with one of the claims 1 to 6 characterised by a large nozzle (60) for the supply of the protective gas (77), within which space is provided for the laser beam (20) and for a small nozzle (31), with it being possible to supply coating material (30) using the small nozzle and with a movable holder (5) for the workpiece and an induction heating (4, 40) being arranged under the outlet aperture (61) of the large nozzle.
8. Apparatus in accordance with claim 7 characterised in that apparatus parts (31, 22) which are located in the flow of the protective gas (77) are suitably formed so



that a laminar development of the flow (70) of the protective gas is ensured.

9. Apparatus in accordance with claim 7 and claim 8 characterised in that a regulation apparatus is provided, by means of which the process parameters, in particular an advancing speed of the movable holder (5), are regulatable as a result of temperature measurements at and on the workpiece (1).
10. Workpiece (1) manufactured in accordance with the method in accordance with one of the claims 1 to 6 characterised in that materials are chosen for the metallic base material (1') and the ceramic coating material (30) for which the coefficients of thermal expansion and the melting temperature each have values which do not differ from one another by more than about 50%, preferably by 20%.
11. Workpiece in accordance with claim 10 characterised in that the base material (1') is a ferritic steel for which a low carbon content is provided in order to largely avoid a Martensite formation.
12. Workpiece in accordance with claim 10 or claim 11 characterised in that the coating material (30) consists of a mixture of Al_2O_3 and ZrO_2 , in particular a eutectically solidifying Al_2O_3 - ZrO_2 alloy, which can additionally contain for example chromium, titanium, yttrium, magnesium and/or calcium oxide, with a maximum of 10 percent by weight of the additional oxides.
13. Workpiece in accordance with one of the claims 10 to 12 characterised in that the ceramic coating material



(30) additionally contains up to 40 percent by volume of particles which are chemically largely stable with respect to the liquid melt phases arising in the coating procedure, with the particles consisting of hard ceramic materials such as carbides, nitrides, borides and/or oxides or being enveloped by resistant protective layers.

14. Workpiece in accordance with one of the claims 10 to 13 characterised in that the adhesion producing layer (11) or the alloy additive contains reactive elements, for example Ti, in metallic form.

