US 20140186540A1

(19) **United States**

(12) **Patent Application Publication**

Schramm et al.

(10) **Pub. No.: US 2014/0186540 A1**

(43) **Pub. Date: Jul. 3, 2014**

(54) **PLASMA SPRAYING PROCESS**

(71) Applicant: **Ford Global Technologies, LLC**, Dearborn, MI (US)

(72) Inventors: **Leander Schramm**, Remda-Teichel OT Teichroeda (DE); **Clemens Maria Verpoort**, Monheim am Rhein (DE); **Alexander Schwenk**, Wohlen (CH); **Enrico Hauser**, Langenbach b.K. (DE)

(73) Assignee: **Ford Global Technologies, LLC**

(21) Appl. No.: **14/237,545**

(22) PCT Filed: **Sep. 27, 2012**

(86) PCT No.: **PCT/EP2012/069021**

§ 371 (c)(1), (2), (4) Date: **Feb. 6, 2014**

(30) **Foreign Application Priority Data**

Oct. 17, 2011 (DE) 10 2011 084 608.5

Publication Classification

(51) **Int. Cl.**

C23C 4/08 (2006.01)

C23C 4/12 (2006.01)

(52) **U.S. Cl.**

CPC .. ***C23C 4/08*** (2013.01); ***C23C 4/125*** (2013.01)

USPC **427/449**

(57) **ABSTRACT**

The application relates to a process for producing a coating by thermal spraying, in particular by plasma spraying, in which a component, in particular a cylinder liner, is internally coated with an alloy. It is proposed that nitrogen is fed as transporting gas, a spraying additive being a solid alloy wire which is guided into a plasma stream, and coating being performed without additional powder.

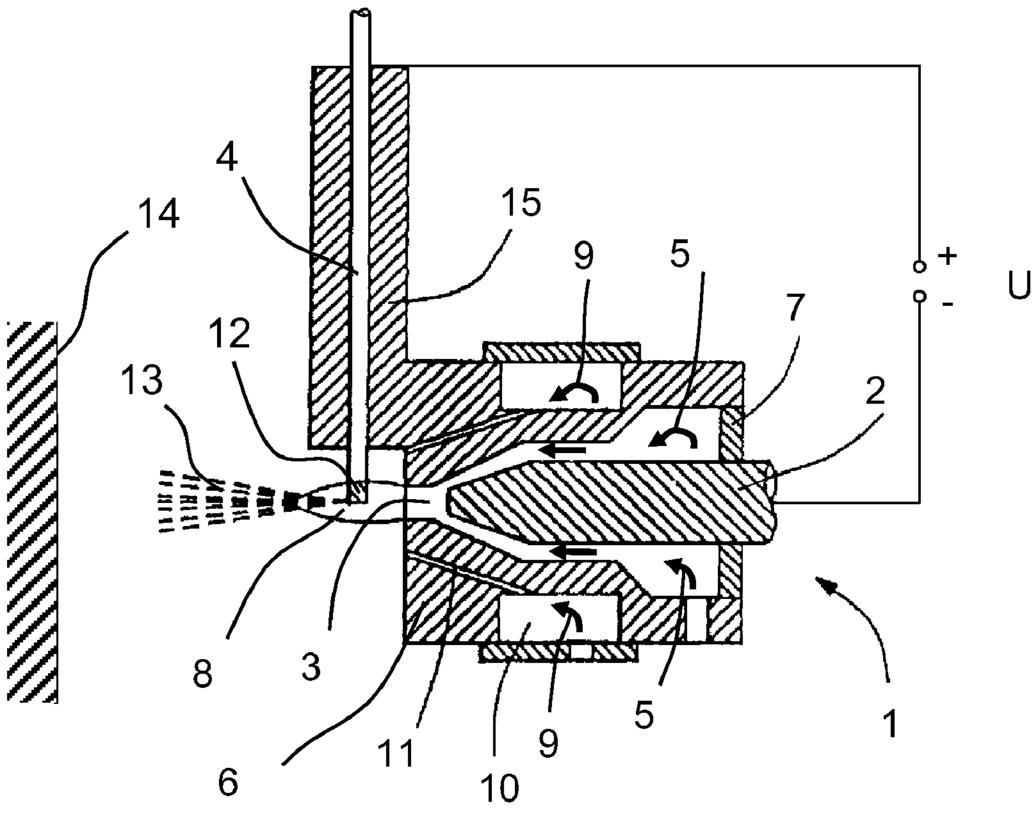
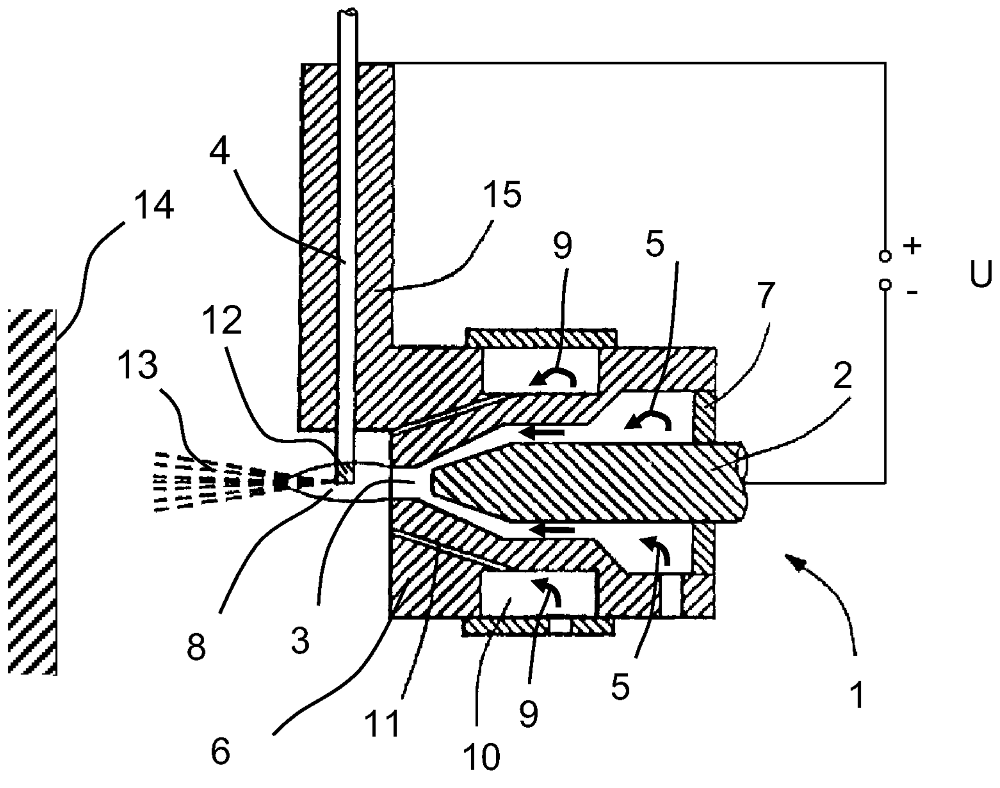


Fig. 1



PLASMA SPRAYING PROCESS

[0001] The present invention relates to a process for producing a coating by thermal spraying, in particular by plasma spraying, in which a component, in particular a cylinder liner of an internal combustion engine, which is produced for example from aluminum, is coated with an alloy, preferably with an iron alloy.

[0002] It is known from EP 1 967 601 A2 to coat, for example, an aluminum engine block, in particular the cylinder bearing surface thereof, with an iron alloy by carrying out arc wire spraying. In this respect, EP 1 967 601 A2 proposes the use of an iron alloy which contains, inter alia, 5 to 25% by weight chromium. It is essential in the case of EP 1 967 601 A2 that an additional powder, to be precise boron carbide, is additionally fed to the iron melt. The arc wire spraying process of EP 1 967 601 A2 involves what is known as the TWAS process, in which two wires are fed to a spray head in such a manner that the power is transmitted across the wires. If the two wires make contact, an arc which melts the wires is formed by a permanent short circuit. A nozzle from which compressed air or an inert gas such as nitrogen is discharged is located downstream of the nozzle. This gas stream atomizes the molten iron alloy and feeds it together with the molten boron carbide powder to the surface to be coated.

[0003] DE 44 11 296 A1 and DE 44 47 514 A1 are concerned with coatings provided by means of plasma spraying, in which however a metal powder or a filler wire are melted and in which nitrogen is fed to the material mixture by means of metallic nitrogen compounds in order to harden the coating.

[0004] Present-day internal combustion engines and the engine blocks thereof can be cast from a metal or aluminum, aluminum blocks in particular having an iron or metal layer on the cylinder bores thereof. The metal layer can be sprayed on by thermal processes. The processes mentioned above are known as thermal spraying processes.

[0005] What is termed the PTWA (Plasma Transfer Wire Arc) internal coating process is also known. In this process, bores (cylinder bores) can be coated from the inside with a wire-like spraying additive. Here, therefore, only a single wire-like spraying additive is supplied, it being possible to use a filler wire or else to supply spraying powder. The plasma impinges on the preheated, wire-like spraying additive. The plasma gas is usually an argon-hydrogen mixture. In the PTWA process, air or compressed air is used as the transporting gas or atomizer gas. The layers which are produced by this process are distinguished by a low porosity. The PTWA internal coating process has proven suitable to date for the internal coating of cylinder bores.

[0006] However, it has been found that the metal or iron coatings produced by the coating processes possible to date for the cylinder bores do not withstand the particular corrosion conditions of ethanol-containing fuels or ethanol fuels. This is observed particularly when the motor vehicle or the internal combustion engine is not used for a relatively long time, which may be the case for example when it is switched off during a vacation. Even an alloy containing 17% by weight chromium had traces of corrosive attack on the protective coating.

[0007] Proceeding from the identified problem of corrosion caused by ethanol-containing fuels on metal coatings of cylinder bores, the invention is based on the object of specifying a process of the type mentioned in the introduction which makes it possible to produce a coating which is improved in this respect.

[0008] According to the invention, the object is achieved by a process having the features of claim **1**. Further particularly advantageous refinements of the invention are disclosed in the subclaims.

[0009] It is pointed out that the features specified individually in the following description may be combined with one another in any desired technically meaningful way and disclose further refinements of the invention.

[0010] The invention proposes a process for producing a coating by thermal spraying, in particular by plasma spraying, in which a component, in particular a cylinder liner of an internal combustion engine, which is produced or cast from aluminum, is coated with an alloy, in which process nitrogen is fed at least as transporting gas, a spraying additive being a solid alloy wire which is guided into a plasma stream, and coating being performed without additional powder or without powder. It is advantageous if the plasma spraying is PTWA (Plasma Transfer Wire Arc) internal coating.

[0011] Within the context of the invention, the term "without additional powder" or "without powder" means that neither a filler wire filled with (metal) powder nor a separately fed (metal) powder is used. Specifically, in the invention, use is advantageously made merely of a solid, i.e. homogeneous or an unfilled additional spraying wire. A suitable alloy for coating comprises chromium as alloying element and mainly iron. A preferred metal or iron alloy is disclosed further below.

[0012] On account of the advantageous use of nitrogen gas as transporting gas instead of air or instead of compressed air, as is used for example in the known PTWA process, the transformation or the degradation of the chromium caused by the oxygen in the air used to date is precluded, and therefore the entire chromium proportion of the alloy can be used to form a stable protective layer. On account of the difference in the free enthalpy (or the Gibbs free energy), predominantly aluminum nitrides rather than chromium nitrides are formed. These aluminum nitrides replace the existing wear-resistant metal oxides which form during the PTWA spraying process with compressed air. As a result, the invention thus gives rise not only to a wear-resistant coating, but also to a protective (anti-corrosion) layer which withstands the corrosive attacks in particular by ethanol-containing fuels. Within the context of the invention, ethanol-containing fuels for internal combustion engines can contain conventional fossil fuel (e.g. E5, E10 or E85) as an admixture of ethanol, or can be used in pure form (E100).

[0013] In the PTWA process known to date, it was assumed that an alloy comprising 17% by weight Cr is particularly suitable for meeting the requirements. By contrast, it is expediently provided in the invention that the additional spraying wire comprises an iron alloy with a chromium proportion of 12 to 35% by weight. Further alloying constituents can be aluminum (2-10% by weight), silicon (0-1% by weight), manganese (0-1% by weight), carbon (0-1% by weight) and further constituents such as, for example, phosphorus (0-1% by weight), sulfur (0-0.09% by weight), molybdenum (0-5% by weight), nickel (0-1% by weight), copper (0-0.5% by weight), nitrogen (0-0.5% by weight), the remainder being iron.

[0014] In a particularly preferred embodiment, the additional spraying wire comprises, according to the invention, an iron alloy comprising 23% by weight Cr, 5% by weight Al, less than 0.5% by weight Si, less than 0.2% by weight Mn, less than 0.05% by weight C, the remaining constituents having a proportion of less than 2% by weight, and the remainder being iron.

[0015] It goes without saying that the process according to the invention can also be used for coating other components.

[0016] FIG. **1** shows a nozzle unit **1** of a PTWA internal coating apparatus. The PTWA (Plasma Transferred Wire Arc) coating system is a system for coating bores, in particular cylinders in engine blocks of internal combustion engines. The nozzle unit **1** consists of a cathode **2**, a plasma nozzle **3** and the electrically conductive alloy wire **4** as anode, which is fed perpendicularly to the plasma nozzle **3**. The material used for the cathode **2** is preferably tungsten, which may also be doped with thorium, for example. The plasma gas **5**, for example a mixture of argon and hydrogen, is fed through bores made in the nozzle body **6** and lying tangentially to the circumference. The cathode holder **7** isolates the cathode **2** from the nozzle body **6**. The alloy wire **4** is guided in the wire feed **15** such that it can move in rotation and be displaced longitudinally.

[0017] The process is started by a high-voltage discharge, which ionizes and dissociates the plasma gas **5** between alloy wire **4**, nozzle body **6** and cathode **2**. The thus produced plasma flows through the plasma nozzle **3** at high speed. In the process, the plasma gas **5** is transported toward the alloy wire **4** fed continuously perpendicularly to the nozzle **3**, as a result of which the electric circuit is completed.

[0018] In addition, a transporting gas **9** or an atomizer gas **9** is fed via feed ducts **10** and auxiliary nozzles **11** to the plasma jet **8** emerging from the pilot nozzle **3**.

[0019] The melting and the atomization of the alloy wire **4** are influenced in this case by two phenomena. The wire **4** is firstly resistance heated by large current intensities, which are typically 65-90 amperes. The impact of the plasma jet **8** on the preheated wire **4** ensures that the latter melts at the wire end **12**. In other words, a plasma is generated inside the plasma nozzle **3** by means of high-voltage discharge. A targeted nitrogen gas flow, i.e. the transporting gas **9**, along the discharge path transports the plasma and the molten spraying material **13** onto the surface **14** of the workpiece to be coated.

1. A process for producing a coating by thermal spraying including by plasma spraying, comprising:
coating with an alloy a component, wherein
nitrogen gas is fed at least as transporting gas, a spraying additive being a solid alloy wire which is guided into a plasma stream, and coating being performed without additional powder.

2. The process as claimed in claim **1**, wherein
the plasma spraying is a PTWA coating process, and wherein the component is a cylinder bearing surface.

3. The process as claimed in claim **1**, wherein
the additional spraying wire is an iron alloy comprising 12 to 35% by weight Cr, 2-10% by weight Al, 0-1% by weight Si, 0-1% by weight Mn, 0-1% by weight C.

4. The process as claimed in claim **3**, wherein the iron alloy further comprises constituents including 0-1% by weight P, 0-0.09% by weight S, 0-5% by weight Mo, 0-1% by weight Ni, 0-0.5% by weight Cu, 0-0.5% by weight N, and a remainder Fe.

5. The process as claimed in claim **1**, wherein
the additional spraying wire is an iron alloy comprising 23% by weight Cr, 5% by weight Al, less than 0.5% by weight Si, less than 0.2% by weight Mn, less than 0.05% by weight C, and remaining constituents having a proportion of less than 2% by weight, a remainder being iron.

6. The process as claimed in claim **1**, wherein the component is an internal combustion engine component.

7. The process as claimed in claim **6**, wherein the component is cast aluminum.

8. The process as claimed in claim **6**, wherein the transporting gas is air.

9. The process as claimed in claim **6**, wherein the solid alloy wire is homogeneous.

10. The process as claimed in claim **6**, further comprising operating the engine with ethanol containing fuel.

11. A process, comprising:
producing a coating by thermal spraying, including by plasma spraying, including coating an engine cylinder bearing surface with an alloy, where nitrogen gas is fed at least as transporting gas, a spraying additive being a solid alloy wire which is guided into a plasma stream, and coating being performed without additional powder, wherein the plasma spraying is a PTWA coating process.

12. The process as claimed in claim **11**, wherein the cylinder bearing surface is cast aluminum, the engine being configured to combust ethanol-containing fuel.

13. The process as claimed in claim **12**, wherein the transporting gas is air.

14. The process as claimed in claim **13**, wherein the solid alloy wire is homogeneous.

15. The process as claimed in claim **14**, further comprising operating the engine with ethanol-containing fuel.

* * * * *