

Thermal spray powder for sliding systems which are subject to heavy loads

5 The present invention relates to a process for producing chromium nitride-containing spraying powder, a chromium nitride-containing spraying powder which is obtainable by such a process and also a process for producing a surface-coated component by thermal coating of the component by means of the powder. The invention further relates to a coated component obtainable by such
10 a coating process and also the use of the powder for the surface coating of components, in particular components in piston machines, for example piston rings or other, tribologically stressed components such as hydraulic cylinders.

Tribologically stressed parts of this type are provided with coatings in order to
15 improve the tribological and wear properties. Coatings are characterized, in a manner analogous to massive materials, by various properties which can be determined empirically. These include, for example, hardness, wear resistance and corrosion resistance in various environments or workability. Customary spraying processes are, for example, thermal spraying, laser cladding and
20 physical or chemical vapor deposition (PVD, CVD).

However, in many applications, the frictional behavior of coatings relative to a second friction partner plays a particular role. Examples are coated piston rods which run in a guide sheath made of steel or cast iron. The behavior of the
25 friction pairing "coating/friction partner" is of great importance, for example in internal combustion engines where coated piston rings run in a bushing made of, for example, gray cast iron or AISi alloys. In particular in such applications, CrN has been found to be particularly useful. Coatings composed of or containing CrN are therefore widely applied by PVD (physical vapor deposition) to piston rings
30 for internal combustion engines, piston compressors and similar piston machines, but also to extruder screws and similar components, for example for plastics processing or nonferrous metal working. Such layers allow good running performance or operating lives (lifetimes) with minimal wear and have become established, for example, in the passenger car sector. However, a disadvantage

is a high capital outlay for plant engineering, which is economical only in the case of large quantities and components having small dimensions. In the case of components having relatively large dimensions or thicker layers, it was hitherto not possible to apply CrN economically by means of PVD. In addition, stresses due to different coefficients of thermal expansion of substrate to be coated and layer material occur in PVD layers having increasing layer thickness. Such stresses lead to crack formation through to detachment of the layer. As a result, there is not a sufficient wear reserve for many uses in highly stressed friction pairings due to an insufficient layer thickness.

Thermal spraying is a possible alternative to PVD for producing coatings. Coatings produced by thermal spraying can have a layer thickness up to several 100 μm .

For the purposes of the present invention, thermal spraying is application of a material to a usually metallic surface, in which the material is, before impingement on the surface, conveyed into an energy source, usually a burner flame or plasma flame, and melts completely or partly due to the thermal energy of the energy source and also experiences acceleration in the direction of the substrate surface as a result of the kinetic energy of the gas stream. When powders are applied directly to the substrate by means of a thermal spraying process, these are referred to as thermal spraying powders.

Customary thermal spraying processes are, for example, high-energy flame spraying using air or oxygen, plasma spraying or electric arc spraying of powders or powder-filled wires. Here, pulverulent particles are introduced into a combustion flame or plasma flame which is directed at the (usually metallic) substrate which is to be coated. Thereby, the particles melt completely or partly in the flame, impinge on the substrate, solidify there and form the coating in the form of solidified flat particles (known as "splats"). The processes mentioned make it possible to apply coatings having a thickness of from about 50 μm to about 2000 μm and allow optimal layers to be developed for particular uses by targeted selection of process and powder.

Coatings produced by such processes, known as thick layers, often consist of one or more usually ceramic and/or metallic components. Here, the metallic component is able to dissipate stresses in the layer by elastic deformation or plastic flow, while the ceramic hard phase gives optimal wear behavior of the layer. Good layer quality is characterized by a largely homogeneous distribution of the individual components and by a low porosity. In addition, there are requirements defined by the respective use, for example in respect of wear resistance and/or corrosion resistance.

Powders for thermal coating, hereinafter referred to as "spraying powders" can, depending on the production process, be present in various forms. Customary forms are, for example, "agglomerated/sintered" or "densely sintered", "melted", "gas-atomized or water-atomized". The typical internal structure of such forms can be seen from DIN EN 1274.

In addition, spraying powders having differing natures can be mixed. However, such "blends" lead to inhomogeneous distribution of the individual components in the layer, which is disadvantageous for many uses. In addition, demixing (segregation) can occur during powder transport and during spraying, and the composition of the layer can therefore differ locally from the composition of the powder mixture.

The use of agglomerated and subsequently intrinsically sintered (sintered together in itself) spraying powders ("agglomerated/sintered spraying powders") composed of different individual components enables the layer homogeneity to be substantially improved since the use of fine individual components enables optimum distribution of the individual constituents in the sintered pellets and in the sprayed layer to be achieved. Agglomeration is usually effected by spray drying an aqueous suspension of the individual components. Selection of the process parameters during agglomeration makes it possible to set the grain size distribution in a targeted manner and adapt it to the spraying system. The impingement efficiency can be substantially improved by means of optimal spraying parameters.

In addition, agglomerated/sintered spraying powders or sintered spraying powders offer the advantage of setting the composition of the layer in a targeted manner by selection of the individual components. Agglomerated/sintered spraying powders based on, for example, WC-Co(-Cr) or Cr₃C₂-NiCr are widespread.

Compared to agglomerated/sintered spraying powders, atomized powders have a more uniform composition than agglomerated/sintered spraying powders since they are formed from a homogeneous melt. Atomized powders are produced by making available the components in nonoxidic form (these can be, for example, metals, ferrous alloys, graphite, master alloys and others), melting them together and then atomizing the melt to produce droplets. The droplets cool during flight through a protective gas atmosphere or are solidified in water and are subsequently collected. While water-atomized powders have a splat-like morphology due to their sudden cooling, gas-atomized powders typically have a good spherical shape.

As in the case of agglomeration, selection of the process parameters during atomization likewise makes it possible to set the grain size distribution in a targeted manner. Owing to the spherical particle shape of gas-atomized alloys, these are often free-flowing and can be transported and processed advantageously. Customary spraying processes for atomized powders are, for example, plasma spraying and high-energy flame spraying.

Compared to agglomerated/sintered spraying powders, individual particles of atomized powders have barely any internal porosity. Layers produced from atomized spraying powders are more homogeneous and have a lower porosity than comparable layers produced from agglomerated/sintered spraying powders. Since atomized powders are obtained from a homogeneous melt, the ability to produce composite powders composed of a plurality of components is greatly restricted in this way.

Thermal spraying layers based on Cr₃C₂ or based on Mo₂C in combination with metals and alloys such as Ni, Mo or NiCr or spontaneously flowing alloys such as

NiCrBSi or combinations thereof are widespread prior art within tribological systems, for example within hydraulic cylinders or piston machines. Agglomerated/sintered spraying powders are usually used, but blends are occasionally also used.

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EP0960954B1 discloses a powder which consists essentially of Cr, Ni and C and has been produced by gas atomization in combination with subsequent heat treatment to precipitate carbides.

- 10 DE102008064190A1 discloses a process for producing a water-atomized Fe-based powder which is suitable for thermal spraying and has a carbon content of 4-9% and also, inter alia, Si as further constituent. Such a powder contains fine carbide and silicide precipitates as hard material constituent, but nitrogen only as constituent of the alloy and not as hard material constituent. A further
- 15 disadvantage is that the thermal sprayability is brought about by means of a subsequent mechanical or thermal treatment in which the chromium nitrides according to this patent application are degraded. However, further atomized powders having incorporated hard material constituents and in particular nitrides as hard material phase are not known.

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- Owing to its molecular structure and the associated pronounced chemical inertness, CrN has excellent resistance to frictional wear and also microwelding. This also applies in corrosive environments and in the presence of lubricants. For this reason, forming tools, for example, composed of cold working steels or, for
- 25 example, tools for plastics processing are often provided with a thin layer of CrN or Cr₂N. Such layers applied by PVD, known as thin layers, display excellent wear resistance, for example in the working of nonferrous metals, and often allow minimal quantity lubrication or a change to aqueous emulsions as lubricating medium. Thin layers applied by PVD usually have a typical thickness of only
- 30 about 2-10 µm. With increasing layer thickness, the residual compressive stresses in the layer also increase. When the residual compressive stresses in the layer approach the adhesive strength of the layer, detachment of the layer (delamination) or spalling of the layer can occur. Residual stresses can be

reduced by application of a plurality of structured sublayers, by which means layers of $> 10 \mu\text{m}$ can be applied with sufficient adhesive strength via PVD.

EP1774053B1 discloses a process for producing a coating on a piston ring, which coating allows application of relatively thick CrN layers by means of a modified PVD process. This is said to make it possible to produce layer thicknesses in the range from 10 to 80 μm .

Thin layers are also known into which fine dispersoids consisting of nickel have been introduced so as to dissipate residual stresses in the layer by elastic deformation or plastic flow and thus decrease the hardness of the layer in a targeted manner (A Plasma assisted MOCVD Process for synthesis of CrN/Ni Composite Coatings, A.Dasgupta, P.Kuppusami, IGCAR).

Furthermore, Ni-CrN(Cr₂N) PVD composite layers are known which are used, inter alia, as an alternative to electrolytically deposited hard chromium layers.

A disadvantage of PVD processes is the restriction to substrates having limited dimensions since the PVD coating process takes place in a closed oven. In addition, the process is very time-consuming, in particular in the case of structured or multilayer coatings. For this reason, the production and repair of layers via PVD is very costly. In addition, in-situ repair of PVD layers is usually not possible since a PVD layer can, in contrast to thermal spraying layers, only be freshly built up in its entirety in the case of a repair, which drastically increases the outage times and in many cases cannot be carried out economically.

In practice, the low thickness of the PVD layers is sometimes particularly disadvantageous, which can mean that the wear reserve is not sufficient for relatively long operating lives,.

To overcome these disadvantages, a thermally sprayed layer based on chromium nitrides would be advantageous. The basis for such a layer would be a spraying powder which contains chromium nitrides and a metallic fraction as ductile

component to dissipate stresses in the layer and which can at the same time be processed to give high-quality layers.

Such spraying powders are not available according to the present prior art.

- 5 DE 10 2008 056 720 B3 relates to a coated sliding element which serves as piston ring in an internal combustion engine. The coating concerned is based on CrN-containing spraying powders, the production process for which is not disclosed. The state of the art for piston ring coatings is blends of one or more ceramic components and one or more metallic components (DE69605270T2).

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- The sliding layer mentioned in DE 10 2008 056 720 B3 has a nominal composition of from 10 to 30% of Ni, from 0.1 to 5% of carbon, from 10 to 20% of nitrogen and from 40 to 79.9% of chromium. The spraying powder described in the working example has a nominal composition of 60% of CrN, 10% of Cr₃C₂,
15 25% of Ni and 5% of Cr. The homogeneous distribution of the carbides (the 10% of Cr₃C₂ present in the spraying powder) in the sprayed layer is described. The size and distribution of the CrN is not disclosed.

- It is an object of the present invention to solve the abovementioned problems of
20 the prior art. In particular, it was an object of the present invention to provide a spraying powder which allows the production of layers having a high density and layer homogeneity and which has good processing properties as thermal spraying powder as well as chromium nitrides as hard material phase.

- 25 It has been found that a solution to the problem can be achieved in the production of a chromium nitride-containing spraying powder, in which a chromium-containing alloy powder is nitrified in the presence of nitrogen with formation of CrN and/or Cr₂N.

- 30 The present invention provides a process for producing chromium nitride-containing spraying powder, which comprises the following steps:

- a) production or provision of an alloy powder comprising
 - i) at least 10% by weight of chromium and

- ii) at least 10% by weight of one or more further elements (A) selected from transition groups IIIA to IIB of the Periodic Table and also B, Si, Ti, Ga, C, Ge, P and S,

b) nitriding of the powder in the presence of nitrogen with formation of CrN and/or Cr₂N.

In a preferred embodiment of the invention, the process comprises the following steps (the steps a-1) and a-2) are substeps of step a)):

10 a-1) production of a melt comprising

- i) at least 10% by weight of chromium and
- ii) at least 10% by weight of one or more further elements (A) selected from transition groups IIIA to IIB of the Periodic Table and also B, Si, Ti, Ga, C, Ge, P and S,

15 a-2) atomization of the melt produced in step a-1) to form an alloy powder and

b) nitriding of the powder in the presence of nitrogen with formation of CrN and/or Cr₂N.

In an embodiment, the alloy powder and the melt from which the alloy powder is produced by atomization comprises at least 10% by weight of chromium and at least 10% by weight of one or more elements (A) selected from transition groups IIIA to IIB of the Periodic Table (IUPAC system, corresponding to CAS system IIIB to IIB) and aluminum.

25 The proportion of chromium in the alloy powder is important especially because a reaction of the chromium present in the alloy powder to form CrN and/or Cr₂N takes place in the subsequent nitriding step b).

In a preferred embodiment of the present invention, the alloy powder comprises chromium in an amount of 30-95% by weight, preferably 40-90% by weight, in particular 45-75% by weight, in each case based on the total weight of the alloy powder.

In a further preferred embodiment, the remaining metals of the alloy powder (i.e. all metals apart from chromium) or the element(s) (A) are present in an amount of 15-70% by weight, preferably 20-60% by weight and in particular 25-55% by weight, in each case based on the total weight of the alloy powder.

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In an especially preferred embodiment, the element(s) (A) of the alloy powder are selected from among cobalt base alloy or nickel base alloy or iron base alloys, where the base alloy optionally contains one or more constituents selected from the group consisting of Si, Mo, Ti, Ta, Nb, V, S, C, P, Al, B, Y, W, Cu, Zn and Mn.

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The further elements (A), in particular the remaining metals (i.e. all metals apart from chromium), of the alloy powder are preferably present in an amount of 15-70% by weight, preferably 20-60% by weight and in particular 25-55% by weight, in each case based on the total weight of the alloy powder.

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In a further embodiment of the present invention, the weight ratio of chromium to the element(s) (A), in particular the remaining metals, can be from 1:9 to 9:1, preferably from 2:8 to 8:2, more preferably from 3:7 to 7:3 and in particular from 2:3 to 3:2.

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In a further preferred embodiment of the present invention, the alloy powder comprises one or more element(s) selected from the group consisting of Si, V, Mo, Ti, Ta, Nb, Al, B, Y, W, Cu, Zn and Mn in an amount of up to 20% by weight, preferably from 0.1 to 15% by weight, in particular from 0.2 to 10% by weight, especially from 0.5 to 5% by weight, in each case based on the total weight of the alloy powder.

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In a further preferred embodiment, the alloy constituents from which the alloy powder is produced in process step a) are present at least partly in elemental form or as ferrous alloy (ferro alloy).

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The elements (A) serve essentially as metal matrix (binder metal) for the chromium nitrides which are obtained by nitriding of the alloy powder and act as hard materials.

- 5 In a preferred embodiment, the alloy powder comprises a cobalt base alloy or nickel base alloy or iron base alloy. The base alloy can contain one or more constituents selected from the group consisting of Si, Mo, Ti, Ta, V, S, C, P, Al, B, Y, W, Cu, Zn and Mn.
- 10 Depending on the nitriding conditions selected, one or more metals of the alloy powder apart from chromium may be nitrided.

In a particularly preferred embodiment of the process of the invention, the alloy powder comprises a nickel-chromium alloy powder, cobalt-chromium alloy
15 powder or iron-chromium alloy powder.

The production of the alloy powder can be carried out in various ways with which a person skilled in the art will be familiar. The alloy powder can preferably be obtained by comminution of cast pieces.

20 Preference is likewise given to producing the alloy powder by production of a melt comprising

- i) at least 10% by weight of chromium and
25 ii) at least 10% by weight of one or more further metals (A) selected from transition groups IIIA to IIB of the Periodic Table and also B, Al, Si, Ti, Ga, C, Ge, P and S and subsequent atomization of the melt produced to form an alloy powder.

30 The alloy powders produced by means of atomization lead to round and thus readily-flowing powders having a high apparent density. During atomization, the melt is broken up into tiny droplets. The melt can be broken up during atomization by means of a gas jet or water jet. Atomization of the melt using a gas jet is preferred; the gas here comprises essentially protective gases,

preferably essentially nitrogen or argon. The powders produced in this way thus have an extremely low level of impurities.

An inexpensive alternative for producing the alloy powders is water atomization.

5 Here, the gaseous atomization medium, which is used in large amounts and is either lost or has to be worked up in a complicated manner, is replaced by inexpensive water. This makes a continuous mode of operation possible since evacuation and rinsing processes are dispensed with. Water atomization is thus an extremely inexpensive manufacturing process which is particularly
10 advantageous for the production of powders whose cost structure is determined more by processing and personnel costs than by materials costs.

In a further preferred embodiment, the alloy constituents from which the melt is produced in process step a) are at least partly present in elemental form or as ferrous alloy.

15 In a further embodiment of the present invention, atomization is effected by means of a water jet, with the atomization angle α being in the range from 8° to 15° and the atomization pressure preferably being 50-400 bar and the water temperature T preferably being in the range from 10 to 50°C , in particular from
20 15 to 45°C . Setting of these parameters ensures that the droplets of the melt solidify slowly so as to give a round particle shape. In addition, the water is decomposed into its constituents to a lesser degree as a result of the slow cooling, so that a smaller amount of oxides is attached to the powders.

25 The melt preferably has a temperature which is $20\text{-}250^\circ\text{C}$ above the melting point of the alloy.

In a particularly preferred embodiment, atomization is carried out in a protective gas atmosphere which comprises, in particular, argon and/or nitrogen and in
30 which the oxygen content is below 1% by volume, preferably below 0.1% by volume, based on the total volume of the protective gas.

The alloy powder produced or provided in step a) of the process of the invention is nitrided in the presence of nitrogen with formation of CrN and/or Cr₂N in the subsequent step b).

5 Nitriding is diffusion-controlled and can be influenced by the process parameters, in particular by pressure, temperature and hold time during the heat treatment. To form the chromium nitride precipitates after the solubility limit of nitrogen has been exceeded, it is necessary for nitrogen to diffuse into the interior of the particles. To form a covering layer, it is necessary for Cr to diffuse outward and
10 nitrogen at the same time to diffuse into the interior of the particles. The diffusion coefficient of Cr in the particle is dependent exclusively on the temperature, while the diffusion coefficient of N in the particle depends both on the temperature and on the nitrogen partial pressure. The thickness of the covering layer can thus be set via the temperature.

15 Increasing the nitrogen partial pressure thermodynamically favors the formation of CrN, so that the proportion of CrN predominates over Cr₂N. The nature of the precipitates can be controlled by means of the hold time. At a longer hold time, the small precipitates disappear with simultaneous growth of the remaining
20 precipitates.

The nitriding of the alloy powder is preferably carried out in a gas atmosphere containing nitrogen with a partial pressure of greater than 1 bar. Nitriding is preferably carried out as solid-state nitriding, with nitrogen partial pressure and
25 temperature being selected so that formation of or an increase in the amount and, if already present, stabilization of chromium nitrides occurs as a result of nitrogen uptake during nitriding. There is thus no loss of chemically bound nitrogen during nitriding of the alloy powder but rather an increase in the chemically bound nitrogen in the process of the invention.

30 The presence of nitrogen gases in the gas atmosphere during nitriding is essential to the process of the present invention. In an advantageous embodiment, nitriding occurs in a nitrogen-containing gas atmosphere which comprises more than 80% by volume, preferably more than 90% by volume, in

particular more than 98% by volume, of nitrogen, in each case based on the total gas atmosphere.

5 The presence of oxygen is disadvantageous in the process step of nitriding. The presence of oxygen leads to formation of oxides which adversely affect the property profile of the spraying powder. In a preferred embodiment of the process of the invention, nitriding is therefore carried out in a nitrogen-containing gas atmosphere which comprises less than 1% by volume, preferably less than 0.5% by volume, in particular less than 0.05% by volume and
10 especially less than 0.01% by volume, of oxygen, in each case based on the total gas atmosphere.

In addition, it has been found that the pressure of the gas atmosphere during nitriding, in particular during solid-state nitriding, can have a considerable
15 influence on the formation of CrN and/or Cr₂N. The pressure of the gas atmosphere is preferably above 1 bar, for example above 1.5 bar.

Particularly good results can be achieved when nitriding is carried out at a nitrogen partial pressure above 6 bar, preferably in the range from 7 to 100 bar,
20 more preferably 8-15 bar and in particular 9-20 bar.

The higher the nitriding temperature, the higher should the required minimum value for the nitrogen partial pressure be selected.

25 The nitriding, in particular the solid-state nitriding, is preferably carried out at a temperature above 1000°C, preferably in the range from 1050 to 1500°C, more preferably from 1100°C to 1350°C and in particular from 1100°C to 1250°C.

The nitriding, in particular the solid-state nitriding, is usually carried out over a
30 period of at least 1 hour, preferably at least 2 hours, more preferably at least 2.5 hours and in particular in the range from 3 to 48 hours.

In a further embodiment of the present process of the invention, the major part of the sintering bridges which may have been produced during nitriding between the powder particles formed by atomization are broken after nitriding.

- 5 The chromium nitride-containing spraying powders obtainable by the process of the invention have excellent properties. The use of the spraying powders in thermal spraying processes makes it possible to form substantially thicker layers than in comparable PVD processes.
- 10 The present invention further provides a chromium nitride-containing spraying powder obtainable by the process of the invention for producing chromium nitride-containing spraying powder.

The chromium nitride-containing spraying powder of the present invention
15 contains CrN and/or Cr₂N as hard materials.

These hard materials are usually present as disperse hard material precipitates. The hard material precipitates are usually dispersed (disperged) in the particles and surrounded by the metallic matrix, in particular of the further elements (A).

20 The present invention further provides a chromium nitride-containing spraying powder, preferably obtainable by the production process of the invention, which has chromium nitride precipitates having an average diameter of 0.1-20 µm, preferably 0.2-10 µm and in particular 0.4-6 µm (e.g. determined electrooptically
25 as number average by image analysis of (electron) micrographs, for example as Jeffries diameter).

The spraying powder of the invention contains chromium nitride, with CrN preferably being present in an amount of 70% by weight, preferably at least
30 75% by weight, more preferably at least 78% by weight and in particular at least 80% by weight, in each case based on the total weight of chromium nitride in the sintered spraying powder.

In a further preferred embodiment, the spraying powder of the invention is essentially free of carbides and/or borides. For the purposes of the present invention, essentially free means that precipitates of carbides and borides are smaller than 1 μm and are present, in particular, in amounts of less than 0.5% by weight, based on the total weight of the hard materials.

In a further preferred embodiment of the present invention, the spraying powder of the invention has dispersed chromium nitride precipitates.

As an alternative or in addition, the spraying powder of the invention is surrounded by a covering layer of chromium nitrides which preferably have an average layer thickness of 1-8 μm .

In a further preferred embodiment of the present invention, the spraying powder of the invention comprises 50-80% by weight, preferably 55-75% by weight, of chromium nitrides, where the proportion by weight is based on the total weight of the powder.

In a further preferred embodiment of the present invention, the spraying powder of the invention comprises boron and/or sulfur, preferably in an amount of up to 1% by weight.

The spraying powder of the invention can also be a constituent of a blend of various spraying powders.

The invention therefore further provides a spraying powder blend comprising a spraying powder according to the invention. The spraying powder blend preferably comprises one or more spraying powders which is/are different from the spraying powder of the invention.

The chromium nitride-containing spraying powders of the invention and also the spraying powder blends of the invention are particularly suitable for the surface coating of components, for example friction surfaces. The present invention therefore further provides a process for producing a surface-coated component

by coating a component by means of thermal spraying of a spraying powder according to the present invention or a spraying powder blend according to the present invention.

- 5 Thermal spraying can, for example, be carried out by means of high-speed flame spraying or plasma spraying. The components which can be obtained by the coating process have extremely good friction properties. In addition, the spraying process enables the component to be provided with a thicker wear layer compared to conventional layers produced by the PVD process.

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The present invention therefore further provides a coated component obtainable by the coating process of the invention. The coated component preferably has a wear layer which has been obtained by thermal spraying and has a thickness of at least 15 μm , preferably at least 50 μm , in particular at least 100 μm , more
15 preferably at least 200 μm and especially at least 250 μm .

The coated components are preferably piston rings or components in internal combustion engines, piston compressors or piston machines or other tribologically stressed components.

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In a further preferred embodiment, the coated components are forming tools or tools for plastics processing or nonferrous metal working.

- 25 In addition, the present invention further provides for the use of the spraying powder of the invention or of the spraying powder blend of the invention for the surface coating of components, in particular piston rings or components in (internal) combustion engines, piston compressors or piston machines or other, tribologically stressed components.

- 30 In particular, the spraying powder of the invention is used for surface coating by means of thermal spraying, in particular high-speed flame spraying or plasma spraying.

The following examples illustrate the invention without restricting the invention to the examples.

Example 1 (according to the invention):

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A powder having the following composition in percent by weight: 8.86% of N, 43.9% of Ni, 0.41% of C, 0.25% of O was obtained from an atomized alloy which is commercially available (from CuLox Technologies, alloy Ni-Cr 50/50) and consists of about 50 percent by weight of Ni and about 50 percent by weight of
10 Cr by nitriding at a nitrogen partial pressure of 7 bar in a nitrogen gas atmosphere containing less than 0.001% by volume of oxygen at 1160°C for 3 hours.

Figure 1 shows an electron micrograph of the powder obtained in example 1.

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Example 2 (according to the invention):

A powder having the following composition in percent by weight: 9.45% of N, 43.3% of Ni, 0.43% of C, 0.39% of O was obtained from an atomized alloy which is commercially available (from CuLox Technologies, alloy Ni-Cr 50/50) and
20 consists of about 50 percent by weight of Ni and about 50 percent by weight of Cr by nitriding at a nitrogen partial pressure of 11 bar in a nitrogen gas atmosphere containing less than 0.001% by volume of oxygen at 1160°C for 3 hours.

25 Figure 2 shows an electron micrograph of a powder obtained as per example 2.

Example 3 (according to the invention):

A powder having the following composition in percent by weight: 6.61% of N, 44.1% of Ni, 1.59% of C, 1.01% of O was obtained from an atomized alloy which is commercially available (from CuLox Technologies, alloy Ni-Cr 50/50) and
30 consists of about 50 percent by weight of Ni and about 50 percent by weight of Cr by nitriding at a nitrogen partial pressure of 15 bar in a nitrogen gas atmosphere containing less than 0.001% by volume of oxygen at 1160°C for 3 hours.

Figure 3 shows an electron micrograph of a powder obtained as per example 3.

Example 4 (according to the invention):

- 5 A powder having the following composition in percent by weight: 7.32% of N, 44.8% of Ni, 0.63% of C, 0.37% of O was obtained from an atomized alloy which is commercially available (from CuLox Technologies, alloy Ni-Cr 50/50) and consists of about 50 percent by weight of Ni and about 50 percent by weight of Cr by nitriding at a nitrogen partial pressure of 7 bar in a nitrogen gas atmosphere containing less than 0.001% by volume of oxygen at 1200°C for 3 hours.
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Figure 4 shows an electron micrograph of a powder obtained as per example 4.

- 15 Example 5 (according to the invention):

A powder having the following composition in percent by weight: 9.42% of N, 44.4% of Ni, 0.22% of C, 0.37% of O was obtained from an atomized alloy which is commercially available (from CuLox Technologies, alloy Ni-Cr 50/50) and consists of about 50 percent by weight of Ni and about 50 percent by weight of Cr by nitriding at a nitrogen partial pressure of 11 bar in a nitrogen gas atmosphere containing less than 0.001% by volume of oxygen at 1200°C for 3 hours.

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Figure 5 shows an electron micrograph of a powder obtained as per example 5.

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Example 6 (according to the invention):

- A powder having the following composition in percent by weight: 10.3% of N, 43.1% of Ni, 0.17% of C, 0.29% of O was obtained from an atomized alloy which is commercially available (from CuLox Technologies, alloy Ni-Cr 50/50) and consists of about 50 percent by weight of Ni and about 50 percent by weight of Cr by nitriding at a nitrogen partial pressure of 15 bar in a nitrogen gas atmosphere containing less than 0.001% by volume of oxygen at 1200°C for 3 hours.
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Figure 6 shows an electron micrograph of a powder obtained as per example 6.

Example 7 (according to the invention):

A powder having the following composition in percent by weight: 10.49% of N, 42.16% of Co, 0.19% of C, 0.27% of O was obtained from an atomized alloy consisting of about 45 percent by weight of Co and about 55 percent by weight of Cr by nitriding at a nitrogen partial pressure of 11 bar in a nitrogen gas atmosphere containing less than 0.001% by volume of oxygen at 1160°C for 3 hours.

Figure 7 shows an electron micrograph of a powder obtained as per example 7.

Example 8 (not according to the invention):

Atomized alloy powder which was the basis of examples 1 to 6.

It can be seen from figure 8 that the non-nitrided powders have no hard material precipitates of chromium nitrides.

The powders according to the invention are characterized by excellent processing properties. Owing to their largely spherical morphology, the powders according to the invention are free-flowing, and caking in the spray gun is also avoided as a result of the outer shell of CrN. Owing to the largely pore-free morphology of the powders, dense layers can also be sprayed, which effectively prevents substrate corrosion.

Claims

1. Process for producing chromium nitride-containing spraying powder, which comprises the following steps:

5 a) production or provision of an alloy powder comprising

i) at least 10% by weight of chromium and

ii) at least 10% by weight of one or more further elements (A) selected from transition groups IIIA to IIB of the Periodic Table and also B, Al, Si, Ti, Ga, C, Ge, P and S,

10 b) nitriding of the powder in the presence of nitrogen with formation of CrN and/or Cr₂N.

2. Process according to Claim 1, characterized in that the nitriding is carried out at a nitrogen partial pressure of greater than 1 bar.

15 3. Process according to Claim 1 or 2, characterized in that the nitriding is carried out at a nitrogen partial pressure above 6 bar, preferably in the range from 7 to 100 bar, more preferably from 8 to 50 bar and in particular from 9 to 20 bar.

20 4. Process according to one or more of the preceding claims, characterized in that the nitriding is carried out in a nitrogen-containing gas atmosphere comprising less than 1% by volume, preferably less than 0.5% by volume, in particular less than 0.05% by volume, of oxygen, in each case based on the total gas atmosphere.

25 5. Process according to one or more of the preceding claims, characterized in that the nitriding is carried out in a nitrogen-containing gas atmosphere comprising more than 80% by volume, preferably more than 90% by volume, in particular more than 98% by volume, of nitrogen, in each case based on the total gas atmosphere.

30 6. Process according to one or more of the preceding claims, characterized in that the element(s) (A) are selected from among cobalt base alloy or

nickel base alloy or iron base alloys, where the base alloy optionally contains one or more constituents selected from the group consisting of Si, Mo, Ti, Ta, Nb, V, S, C, P, Al, B, Y, W, Cu, Zn and Mn.

- 5 7. Process according to one or more of the preceding claims, characterized in that the nitriding, in particular the solid-state nitriding, is carried out at a temperature above 1000°C, preferably in the range from 1050°C to 1500°C, more preferably from 1100°C to 1350°C and in particular from 1100°C to 1250°C.
- 10 8. Process according to one or more of the preceding claims, characterized in that the nitriding, in particular the solid-state nitriding, is carried out for a period of at least 1 hour, preferably at least 2 hours, more preferably at least 2.5 hours and in particular in the range from 3 to 48 hours.
- 15 9. Process according to one or more of the preceding claims, characterized in that chromium is present in an amount of from 30 to 95% by weight, preferably from 40 to 90% by weight, in particular from 45 to 75% by weight, in each case based on the total weight of the alloy powder.
- 20 10. Process according to one or more of the preceding claims, characterized in that the element(s) (A) is present in an amount of from 15 to 70% by weight, preferably from 20 to 60% by weight and in particular from 25 to 55% by weight, in each case based on the total weight of the alloy powder.
- 25 11. Process according to one or more of the preceding claims, characterized in that the alloy powder comprises one or more additional element(s) selected from the group consisting of Si, V, Mo, Ti, Ta, Nb, Al, B, Y, W and Mn in an amount of up to 20% by weight, preferably from 0.1 to 15% by weight, in particular from 0.2 to 10% by weight, especially from 0.5 to 5% by weight, in each case based on the total alloy powder.
- 30

12. Process according to one or more of the preceding claims, which comprises the following steps:
- 5 a-1) production of a melt comprising
- i) at least 10% by weight of chromium and
- ii) at least 10% by weight of one or more further elements (A) selected from transition groups IIIA to IIB of the Periodic Table and also B, Al, Si, Ti, Ga, C, Ge, P and S,
- a-2) atomization of the melt produced in step a-1) to form an alloy powder and
- 10 b) nitriding of the powder in the presence of nitrogen with formation of CrN and/or Cr₂N.
13. Process according to Claim 12, characterized in that the breaking up of the melt into small droplets during atomization is effected by means of a gas jet or water jet.
- 15 14. Process according to Claim 13, characterized in that the gas of the gas jet comprises essentially protective gases, preferably essentially nitrogen or argon.
- 20 15. Process according to one or more of Claims 12 to 14, characterized in that the melt has a temperature which is from 20 to 250°C above the melting point of the alloy.
- 25 16. Process according to one or more of Claims 12 to 15, characterized in that the alloy constituents from which the melt or the alloy powder is produced in process step a-1) are present at least partly in elemental form or as ferrous alloy.
- 30 17. Process according to one or more of Claims 12 to 16, characterized in that the major part of the sintering bridges which may have been produced during nitriding between the powder particles formed by atomization are broken after nitriding.

18. Chromium nitride-containing spraying powder obtainable by a process according to one or more of Claims 1 to 17.
- 5 19. Chromium nitride-containing spraying powder according to Claim 18, characterized in that the powder contains CrN and/or Cr₂N as hard materials.
- 10 20. Chromium nitride-containing spraying powder, preferably according to Claim 18 or 19, characterized in that it has chromium nitride precipitates having an average diameter of from 0.1 to 20 µm, preferably from 0.2 to 10 µm, in particular from 0.4 to 6 µm.
- 15 21. Spraying powder according to one or more of Claims 18 to 20, characterized in that the nitrided spraying powder contains chromium nitride, with CrN being present in an amount of at least 70% by weight, preferably at least 75% by weight, more preferably at least 78% by weight and in particular at least 80% by weight, in each case based on the total weight of the chromium nitride in the sintered spraying powder.
- 20 22. Spraying powder according to one or more of Claims 18 to 21, characterized in that the spraying powder is essentially free of carbides and borides.
- 25 23. Spraying powder according to one or more of Claims 18 to 22, characterized in that the spraying powder has homogeneously distributed chromium nitride precipitates.
- 30 24. Spraying powder according to one or more of Claims 18 to 23, characterized in that the spraying powder is surrounded by a covering layer of chromium nitrides which preferably has an average layer thickness of from 1 to 8 µm.
25. Spraying powder according to one or more of Claims 18 to 24, characterized in that the powder comprises from 50 to 80% by weight,

preferably from 55 to 75% by weight, of chromium nitrides, where the percentage by weight is based on the total weight of the powder.

- 5 26. Spraying powder according to one or more of Claims 18 to 25, characterized in that the powder contains up to 1% by weight of boron and/or sulfur.
- 10 27. Spraying powder blend comprising a spraying powder according to one or more of Claims 18 to 26.
28. Process for producing a surface-coated component by coating a component by means of thermal spraying of a spraying powder according to any of Claims 18 to 26 or a spraying powder blend according to Claim 27.
- 15 29. Process according to Claim 28, characterized in that the thermal spraying is high-speed flame spraying or plasma spraying.
30. Coated component obtainable by the process according to Claim 28 or 29.
- 20 31. Use of the spraying powder according to any of Claims 18 to 26 or of the spraying powder blend according to Claim 27 for the surface coating of components, in particular piston rings or components in internal combustion engines, piston compressors or piston machines or other, tribologically stressed components.
- 25 32. Use according to Claim 30, characterized in that surface coating is effected by thermal spraying, in particular high-speed flame spraying or plasma spraying.