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(54) Title: HARD METAL COMPOSITION

(57) **Abrégé/Abstract:**

An example process for producing a component which includes sintering a composition including (a) hard material particles comprising an inner core of fused tungsten carbide and an outer shell of tungsten carbide and (b) binder metals selected from the group consisting of Co, Ni, Fe and alloys thereof, wherein sintering is carried out in a temperature range from 1250 °C to 1400 °C over a period of from 3 to 15 minutes and at a gas pressure of less than 10-3 bar, wherein cooling after the sintering operation in the temperature range from sintering temperature to 500 °C is carried out at a cooling rate below 100 K/min characterized in that sintering is carried out with application of a pressing force of from 20 to 80 MPa to the composition, and wherein the content of free carbon in the hard material does not exceed 0.1% by weight.

Abstract

An example process for producing a component which includes sintering a composition including (a) hard material particles comprising an inner core of fused tungsten carbide and an outer shell of tungsten carbide and (b) binder metals selected from the group consisting of Co, Ni, Fe and alloys thereof, wherein sintering is carried out in a temperature range from 1250 °C to 1400 °C over a period of from 3 to 15 minutes and at a gas pressure of less than 10^{-3} bar, wherein cooling after the sintering operation in the temperature range from sintering temperature to 500 °C is carried out at a cooling rate below 100 K/min characterized in that sintering is carried out with application of a pressing force of from 20 to 80 MPa to the composition, and wherein the content of free carbon in the hard material does not exceed 0.1% by weight.

Hard metal composition

Brief Description of Drawings

Figure 1 depicts the microstructure of cemented hard materials comprising fused tungsten carbide (FWC) where the FWC particles have a fine lamellar structure made up of WC and W_2C .

Figure 2 shows a conventional, extra-coarse cemented hard material.

Figure 3 shows the results of wear tests.

The present invention relates to a process for producing a component, which comprises sintering a composition comprising hard material particles and binder metals, and also a component which is obtainable by such a process. In addition, the invention relates to the use of the component under highly erosive and/or abrasive conditions, preferably as chisel in road construction, as part of a drill bit or as wear part, for example as plate for protecting surfaces.

Fused tungsten carbide (FWC) is, owing to its extreme wear resistance, a preferred material for components which are subjected to highly erosive and/or abrasive conditions, e.g. welded wear protection layers or drill bits for oil and gas exploration. The excellent wear resistance of fused tungsten carbide is based on its particular microstructure which is made up of alternating lamellae consisting of tungsten carbide (WC) and ditungsten carbide (W_2C). Fused tungsten carbide is usually processed by infiltration with copper-based solders or welding by means of spontaneously flowing nickel-containing alloys. Owing to the processing by infiltration or by welding, the content of the metallic binder phase is usually 20-40% by weight. In comparison, the binder content (binder = Co or Ni) of commercial WC-Co or WC-Ni cemented hard materials is significantly lower at 3-15%. For the purposes of the present invention, a cemented hard material is a sintered component which comprises essentially a hard material, for example a carbide such as tungsten carbide, and a metallic binder such as cobalt or nickel. Since the wear properties of FWC are significantly superior to WC, there is a demand for fused tungsten carbide for making cemented hard materials having a significantly lower binder content of < 20% industrially usable.

The reason for the lack of usability of fused tungsten carbides in cemented hard materials is essentially that

- a) the fused tungsten carbide particles are dissolved by diffusion in Co in the solid state and also in the liquid phase which arises during sintering and consists essentially of cobalt and/or nickel,
- b) the advantageous lamellar structure is thermally/chemically transformed during the sintering process and
- c) the component cannot be sintered so as to be free of pores.

DE 199 24 683 C2 describes the use of fused tungsten carbide in the head of a round-shaft chisel. In DE 199 24 683 C2, the chisel head is produced by infiltration and not by sintering. It is therefore an object of the present invention to provide a process for producing a pore-free cemented hard material comprising fused tungsten carbide having an intact lamellar structure (called also as feather-like structure) while at the same time using a metallic binder. It has surprisingly been found that fused tungsten carbide can be used as a material for cemented hard materials, provided that they are chemically stabilized and the sintering process is conducted in a specific way. It has surprisingly been found that the transformation of the fused tungsten carbide into macroline FWC consisting of a core of fused tungsten carbide (FWC) and a shell of tungsten carbide (WC) offers sufficient stabilization to produce sintered cemented hard materials. Under appropriate sintering conditions, the WC shell offer sufficient protection against the metallic melt.

In a first embodiment, the present invention provides a process for producing a component, which comprises sintering a composition comprising

- a) hard material particles comprising an inner core of fused tungsten carbide and an outer shell of tungsten carbide and
 - b) binder metals selected from the group consisting of Co, Ni, Fe and alloys thereof comprising at least one metal selected from among Co, Ni and Fe,
- wherein sintering is carried out in a temperature range from 1250°C to 1400°C over a period of from 3 to 15 minutes. Sintering is preferably carried out at a gas pressure below 10^{-2} bar.

An essential constituent of the composition to be sintered is hard material particles comprising an inner core of fused tungsten carbide (FWC) and an outer shell of tungsten carbide (WC). In a preferred embodiment of the present invention, the hard material particle has an inner core of fused tungsten carbide and/or an alloy comprising fused tungsten carbide and at least one further carbide of the elements selected from groups 4B, 5B and 6B of the Periodic Table of the Elements and an outer shell of an alloy comprising tungsten carbide and/or at least one further carbide of the elements selected from groups 4B, 5B and 6B of the Periodic Table of the Elements. If the inner core or the outer shell of the hard material particles consists of an alloy of fused tungsten carbide and a further carbide of the elements selected from groups 4B, 5B and 6B of the Periodic Table of the Elements, i.e. at least one carbide of the elements Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, the total content of further carbides can be up to 10% by weight, based on the hard material particles.

The hard material particles used for the purposes of the invention (hereinafter referred to as "macroline FWC" for short) are, in particular, fused tungsten carbide particles or alloys thereof with at least one carbide of the elements Ti, Zr, Hf, V, Mo, Nb, Ta and Cr and with a shell of tungsten carbide.

Fused tungsten carbide (FWC) is a mixture of w_c and W_2C , which is, in particular, a eutectic microstructure composed of WC and W_2C .

FWC is a eutectic mixture of w_c and ditungsten carbide (W_2C), in which the average carbon mass ratio is generally in the range from 3.8 to 4.2% by weight. This corresponds to a phase distribution of 73-80% by weight of W_2C and 20-27% by weight of WC. FWC has a very fine-grained crystal microstructure which is often described as lamellar structure (called also as feather-like structure) and is obtained by rapid quenching of a carbide melt. The shell of the particles consists of tungsten monocarbide, also referred to as tungsten carbide WC.

WO 2013/060839

- 4 -

PCT/EP2012/071254

A particularly preferred fused tungsten carbide having a WC shell is macroline fused tungsten carbide (MWC, the Amperweld® powder series from H.C. Starck GmbH).

- 5 The hard material used according to the invention, viz. the macroline FWC, can be obtained by transforming FWC into WC by carburization to a desired depth and can generally be used for producing wear protection layers and wear-resistant components.
- 10 The macroline FWC used according to the invention displays, in particular, excellent toughness and hardness of the FWC in the core of the WC/FWC composite which is retained even when it is processed in a conventional way, i.e. brought into contact with a liquid matrix material.
- 15 The hard material used according to the invention preferably has a content of bound carbon of from 4 to 6% by weight, particularly preferably from 4.5 to 5.5% by weight. The content of free carbon should not exceed 0.1% by weight.

- If the content of bound carbon is less than 4% by weight, a sufficiently dense WC
- 20 shell is not formed, so that no increase in the chemical resistance compared to FWC is observed. If the content of bound carbon approaches the limit value of 6.13% by weight corresponding to pure WC, the FWC core becomes so small that an increase in hardness compared to pure WC is no longer achieved.

- 25 The advantageous properties of the hard material powder used according to the invention are also retained when it has a small proportion of WC particles, i.e. not all powder particles are made up of a core of FWC and a WC shell. Such tungsten carbide powders can therefore likewise be used according to the invention.

WO 2013/060839**- 5 -****PCT/EP2012/071254**

Thus, according to the invention, it is also possible to use a powder mixture which consists of tungsten carbide particles and fused tungsten carbide particles having a tungsten carbide shell.

- 5 However, preference is given to at least 70%, in particular at least 80%, advantageously at least 90%, of the powder particles having a core of FWC and a WC shell.

10 The average particle size can vary within a wide range and depends, in particular, on the planned use.

The particle size determined by means of RoTap sieve analysis in accordance with ASTM B 214 can generally be up to 3000 μm . It is advantageous to use a particle size fraction determined by means of RoTap sieve analysis in accordance
15 with ASTM B 214 of from 3 μm to 1500 μm , from 5 μm to 1000 μm , preferably from 5 μm to 500 μm , more preferably from 10 μm to 300 μm or from 10 to 180 μm .

The average particle size can, for example, be set by selection of an FWC powder
20 having a particular average particle size as starting material for producing the macroline FWC. However, it is also possible, for example, to mix particular particle fractions from previously produced macroline FWC or separate off particular fractions, for example by sieving or classifying.

25 In the hard material powder used according to the invention, the FWC core is surrounded by a dense shell of tungsten monocarbide. The thickness of the shell, determined by means of optical microscopy on etched material, is preferably from 0.05 to 0.4 times the average particle size determined by means of RoTap sieve analysis in accordance with ASTM B 214, particularly preferably from 0.05
30 to 0.15 times the average particle size.

WO 2013/060839**- 6 -****PCT/EP2012/071254**

Macroline FWC has excellent hardness. The Vickers hardness is preferably > 2000 HV_{0.1}, particularly preferably > 2500 HV_{0.1}.

5 The morphology of the particles can, for example, be set by use of a suitable FWC powder.

10 The hard material powder used according to the invention can accordingly have various morphologies, for example crushed with sharp edges or spherical. The spherical morphology offers in-principle advantages in respect of the wear resistance, but is more difficult to produce than powder having an irregular morphology. It is also possible to use mixtures of powders of differing morphologies.

15 The hard material powder used according to the invention can be obtained by a process for producing the tungsten carbide according to the invention (macroline FWC), in which fused tungsten carbide powders are heated in the presence of a carbon source to a temperature of from 1300°C to 2000°C, preferably from 1400°C to 1700°C.

20 The process can be carried out in the presence of inert gas, in the presence of reactive gas or under reduced pressure. It is preferably carried out in the presence of hydrogen.

25 A suitable reactive gas is, in particular, a gaseous carbon source, for example carbon monoxide, a CO/CO₂ mixture, a hydrocarbon or a hydrocarbon mixture such as natural gas.

30 Possible carbon sources are gaseous and solid carbon sources. As solid carbon source, it is possible to use, for example, carbon black or graphite. It is naturally also possible to use mixtures of various gaseous and/or solid carbon sources.

WO 2013/060839

- 7 -

PCT/EP2012/071254

The thermal treatment of FWC in the presence of the carbon source results in transformation of FWC into WC at the surface. Thus, a dense WC layer is formed around the FWC.

- 5 Temperature, reaction time and the amount of carbon source added are selected so that the shell of WC is formed with the desired thickness. Care should be taken to ensure that FWC remains in the interior of the particles. The conditions to be adhered to are determined essentially by the particle size and particle shape of the FWC powder used and can be determined by means of simple trials.
- 10 If the carbon content is set too high, this increases the time and temperature required for the reaction and unnecessarily reduces the proportion of the lamellar microstructure, i.e. the proportion of FWC. It has been found to be advantageous to add the carbon source in such an amount that the total carbon content of the reaction mixture, i.e. the sum of the carbon contents of FWC and carbon source,
- 15 is from 4 to 6% by weight, preferably from 4.3 to 5.5% by weight.

- In the reaction of FWC with powder particles having very different particle sizes, relatively fine particle fractions are carburized more strongly in relation to their particle diameter than large particles. This applies particularly to powders having
- 20 a high fines content of $< 45 \mu\text{m}$ and can be prevented by prior removal of the proportion of fines and separate reaction of the various powder fractions. The reaction times are usually from 1 to 10 hours, preferably from 1.5 to 7 hours.

- To produce the component according to the invention, it is possible to use, for
- 25 example, crushed or spherical FWC which is sieved to the desired particle size as starting material. The material is subsequently intimately mixed with a carbon source, e.g. carbon black, in the desired amount, subjected to a heat treatment and in the process carburized on the outer surface layer. The heat treatment can be carried out using conventional tunnel kilns or comparable apparatuses which
- 30 can be operated, for example, in the temperature range between 1550°C and 1900°C under a hydrogen atmosphere or protective gas. The mixture of FWC and carbon black is, for example, placed in graphite boats. In the reaction, the

WO 2013/060839**- 8 -****PCT/EP2012/071254**

carbon reacts with the W_2C present in the FWC and transforms this into WC which can then no longer be distinguished from the WC already present. The WC layer formed in this way forms a natural diffusion barrier for the carbon, so that the desired carburization depth can be controlled via the parameters time and
5 temperature.

A further important constituent of the composition to be sintered according to the process of the invention to produce the component are binder metals. These binder metals are selected from the group consisting of cobalt, nickel and iron
10 and also alloys comprising at least one metal selected from among cobalt, nickel and iron.

Particularly preferred binder metal alloys encompass cobalt and cobalt-nickel alloys having a nickel content of preferably up to 25% by weight.

15

The sintering of the composition comprising the hard material particles and the binder metals is carried out in a temperature range from 1250°C to 1400°C for a period of from 3 to 15 minutes. Sintering is preferably carried out at a reduced gas pressure which is, in particular, below 10^{-2} bar. In a particularly preferred
20 embodiment, sintering is carried out at temperatures of from 1300°C to 1370°C.

It has been found to be advantageous to keep the sintering time as short as possible. In a preferred embodiment, sintering is carried out at the sintering temperatures for a period of from 3 to 10 minutes.

25

According to the invention, sintering is preferably carried out as liquid-phase sintering.

Particularly good results can be achieved when sintering is carried out at a gas
30 pressure of less than 10^{-3} bar, further preferably less than 10^{-4} bar. In a particular embodiment of the process of the invention, heating of the composition up to the desired sintering temperature is carried out at a heating

WO 2013/060839**- 9 -****PCT/EP2012/071254**

rate of above 50 K/min, preferably above 80 K/min, in particular in the range from 90 to 120 K/min. To obtain a pronounced lamellar structure of the hard material particles, it has been found to be particularly advantageous to carry out cooling after the sintering operation, in particular in the temperature range from
5 the sintering temperature to 500°C, at a cooling rate of less than 100 K/min, preferably less than 80 K/min, in particular in the range from 30 K/min to 70 K/min.

It has been found to be advantageous, in particular with a view to achieving
10 essentially pore-free components, to carry out sintering of the composition with the aid of pressure. Here, the application of a pressing force of from 20 to 80 MPa, preferably from 30 to 50 MPa, to the composition to be sintered is particularly useful. Sintering in which an additional pressing force is exerted on the composition gives components which have a reduced number of pores, in
15 particular are essentially pore-free.

The composition to be sintered comprises, in a preferred embodiment, from 60 to 95% by weight, in particular from 70 to 90% by weight, of hard material particles, where the percentages by weight are based on the total weight of the
20 composition.

In a further preferred embodiment, the composition comprises from 5 to 40% by weight, in particular from 10 to 30% by weight, of binder metal, where the percentages by weight are based on the total weight of the composition.

25 The present invention further provides a component which is obtainable by the process of the invention.

In a preferred embodiment, the component has a lamellar structure in the interior of the fused tungsten carbide particles.

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WO 2013/060839

- 10 -

PCT/EP2012/071254

In particular, it has been found that the components of the invention have a microstructure of alternating lamellae consisting of tungsten carbide and ditungsten carbide (W_2C) in the interior of the fused tungsten carbide particles.

- 5 The components of the invention display surprisingly good wear properties.

The present invention therefore further provides for the use of the component of the invention under highly erosive and/or abrasive conditions, preferably as chisel in road construction, as part of a drill bit or as wear part, for example as
10 plate for the protection of surfaces.

Examples

Example 1 (denoted by "Co1" in figure 3):

15

76% by weight of fused tungsten carbide (FWC) [particle size: 150 μm] and 17% by weight of tungsten carbide (WC) [particle size: 6 μm] are sintered together with 15% by weight of cobalt for 3 minutes at 1370°C.

- 20 Sintering is carried out under reduced pressure ($< 10^{-3}$ mbar) and at a pressing force of 45 MPa.

Example 2 (denoted by "Co2" in figure 3):

- 25 72% by weight of FWC (particle size: 300 μm), 18% by weight of WC [particle size: 6 μm] and 10% by weight of cobalt are sintered for 3 minutes at 1320°C under reduced pressure ($< 10^{-3}$ mbar) and at a pressing force of 45 MPa.

Example 3 (denoted by "Co3" in figure 3):

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WO 2013/060839

- 11 -

PCT/EP2012/071254

68% by weight of FWC (particle size: 150 μm), 17% by weight of WC [particle size: 6 μm] and 15% by weight of cobalt are sintered for 3 minutes at 1330°C under reduced pressure ($< 10^{-3}$ mbar) and at a pressing force of 45 MPa.

5

Comparative example (see figure 2):

92% by weight of fused tungsten carbide were sintered together with 8% by weight of cobalt for 45 minutes at 1420°C under reduced pressure.

10

Structure

The microstructure of cemented hard materials comprising fused tungsten carbide (FWC) is characterized by the FWC particles having a fine lamellar structure made up of WC and W_2C (see figure 1). In comparison, figure 2 shows a conventional, extra-coarse cemented hard material.

15

Since the wear properties of FWC are strongly dependent on the fine structure of the lamellae (a coarsened microstructure displays a significant deterioration in the wear properties), densification of the FWC-containing cemented hard material is carried out by means of a brief sintering process in order to retain the fine lamellar structure. Furthermore, the binder content can be set in a controlled manner in the range from 5% to 40% by changing from the infiltration process to the sintering process.

20

25

Wear properties

Figure 3 shows the results of wear tests (ASTM B611-85 (2005)). The particularly small decrease in volume is conspicuous. In the case of the normal, extra-coarse cemented hard materials, which are customarily used in the field of drilling & mining, this is above 300 mm^3 (in accordance with ASTM B611-85).

30

Claims

1. A process for producing a component, which comprises sintering a composition comprising
 - a) hard material particles comprising an inner core of fused tungsten carbide and an outer shell of tungsten carbide and
 - b) binder metals selected from the group consisting of Co, Ni, Fe and alloys thereof,wherein sintering is carried out in a temperature range from 1250 °C to 1400 °C over a period of from 3 to 15 minutes and at a gas pressure of less than 10^{-3} bar, wherein cooling after the sintering operation in the temperature range from sintering temperature to 500 °C is carried out at a cooling rate below 100 K/min characterized in that sintering is carried out with application of a pressing force of from 20 to 80 MPa to the composition, and wherein the content of free carbon in the hard material does not exceed 0.1% by weight.
2. The process as claimed in claim 1, characterized in that the hard material particles have a content of bound carbon of from 4 to 6% by weight, based on the total hard material particles.
3. The process as claimed in either claim 1 or 2, characterized in that the shell of the hard material particles is from 0.05- to 0.4-times the average particle size.
4. The process according to any one of claims 1 to 3, characterized in that sintering is carried out at temperatures of from 1300 to 1370 °C.
5. The process according to any one of claims 1 to 4, characterized in that sintering for a period of from 3 to 10 minutes.
6. The process according to any one of claims 1 to 5, characterized in that sintering is liquid-phase sintering.
7. The process according to any one of claims 1 to 6, characterized in that sintering is carried out at a gas pressure of less than 10^{-4} bar.

8. The process according to any one of claims 1 to 7, characterized in that sintering is carried out by heating at a heating rate above 50 K/min until the desired sintering temperature is attained.

9. The process according to any one of claims 1 to 8, characterized in that cooling after the sintering operation in the temperature range from sintering temperature to 500 °C is carried out at a cooling rate below 80 K/min.

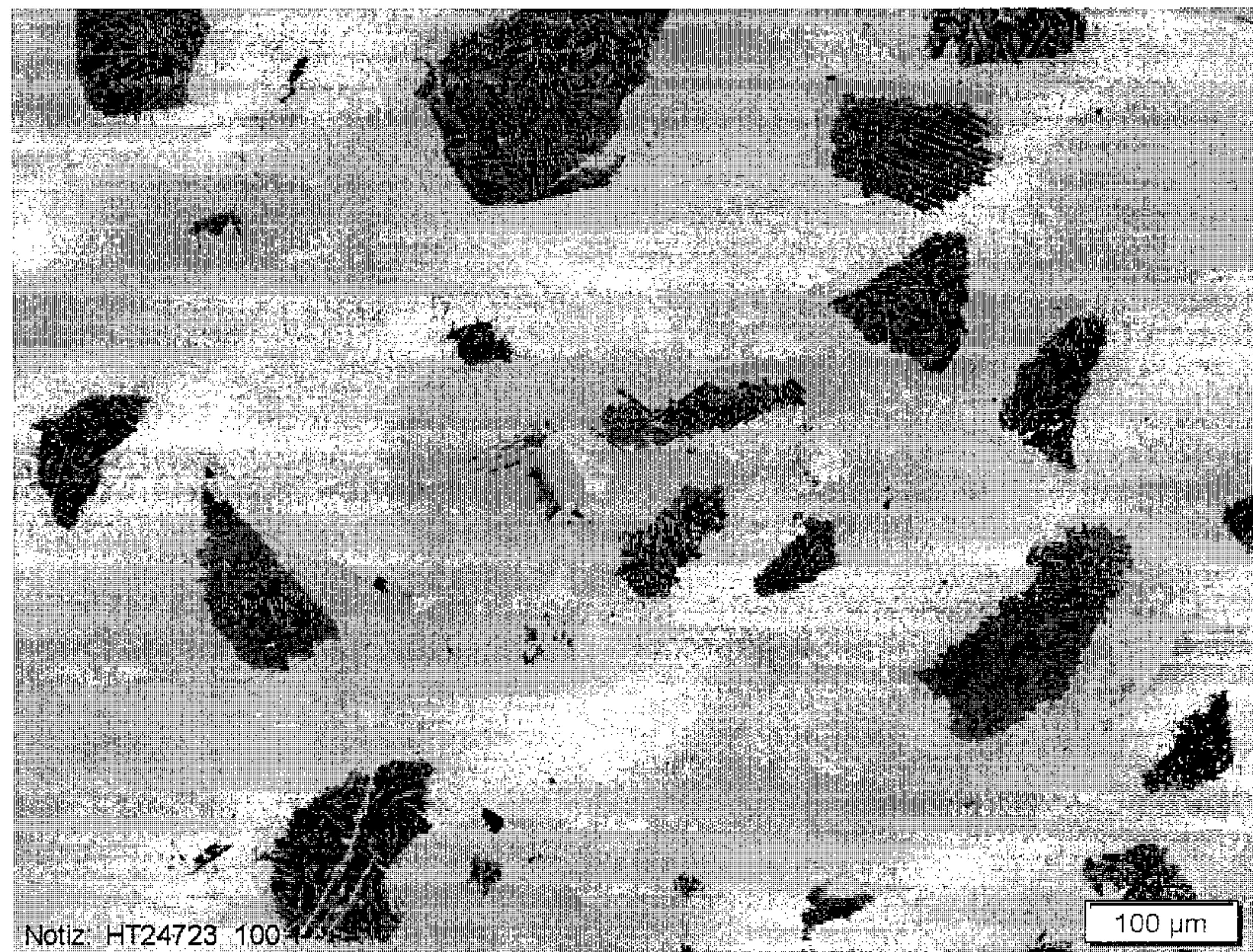
10. The process according to any one of claims 1 to 9, characterized in that the composition comprises from 60 to 95% by weight of hard material particles and from 5 to 40% by weight of binder metal, in each case based on the total weight of the composition.

WO 2013/060839

1/3

PCT/EP2012/071254

Figure 1

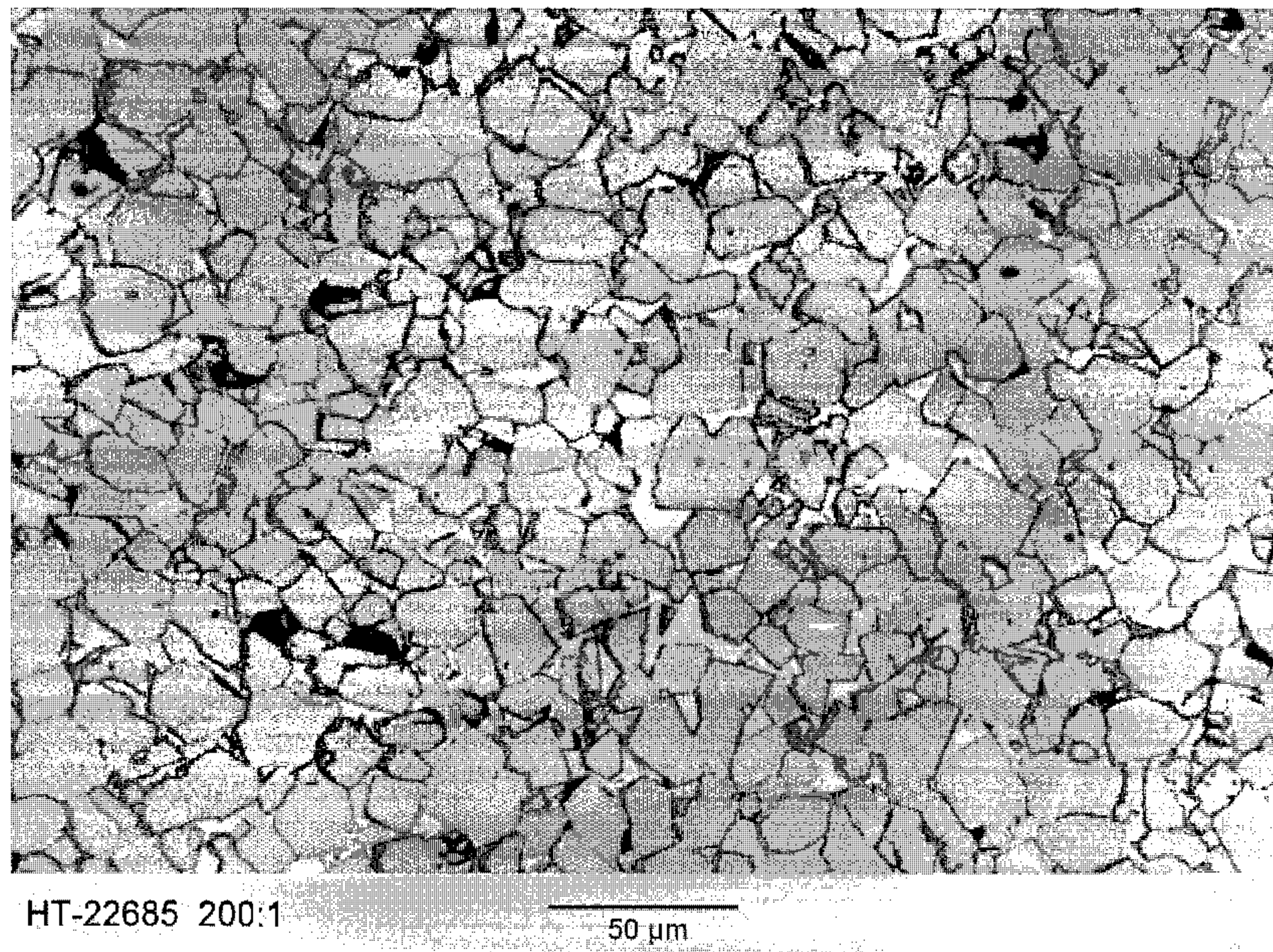


WO2013/060839

2/3

PCT/EP2012/071254

Figure 2



WO2013/060839

3/3

PCT/EP2012/071254

Figure 3

