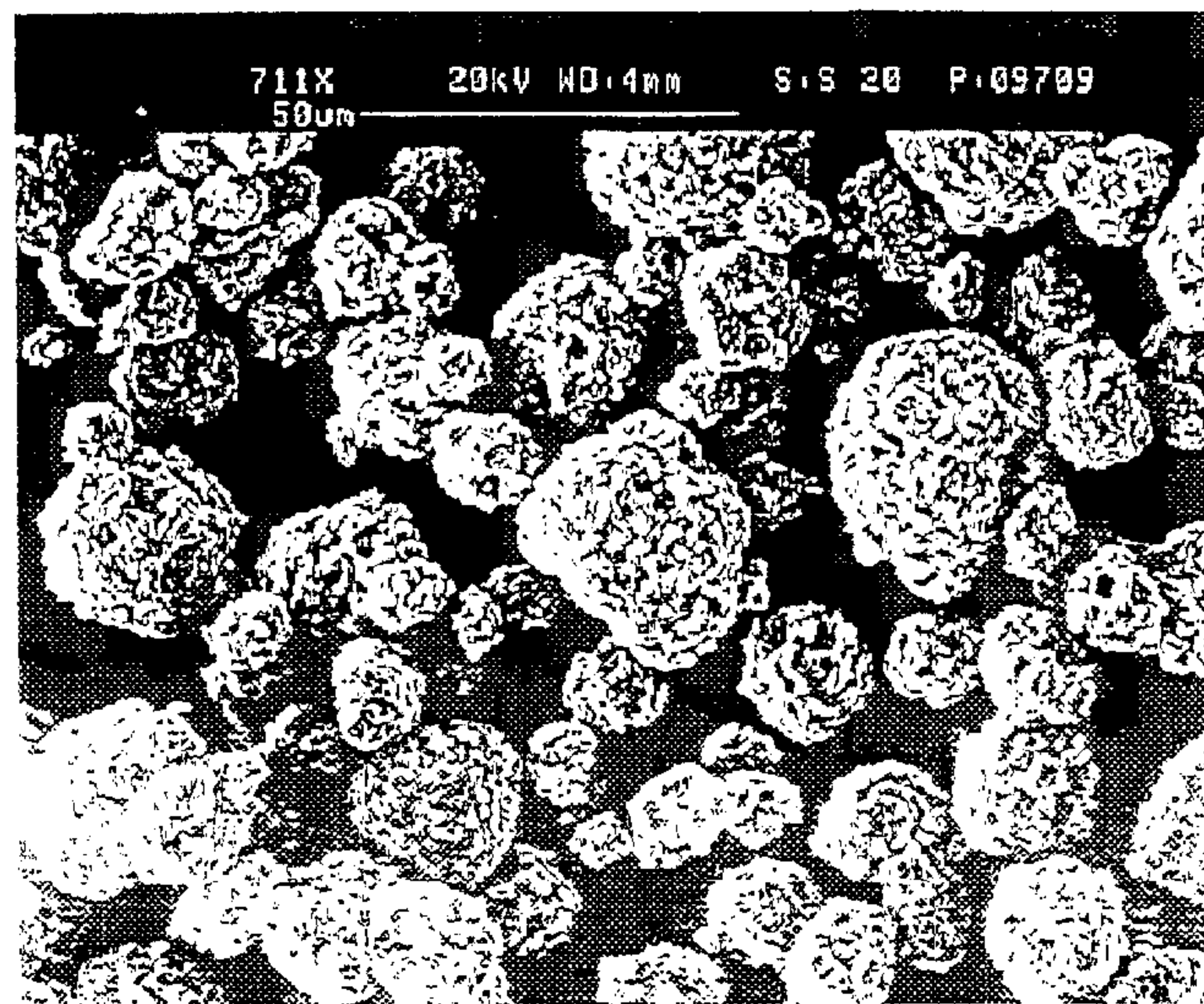




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(54) Titre : POUDRE DE REVETEMENT ET PROCEDE DE PRODUCTION DE LADITE POUDRE
(54) Title: COATING POWDER AND METHOD FOR ITS PRODUCTION



The morphology of the coating powder according to Example
2 (700x enlargement)

(57) **Abrégé/Abstract:**

The invention relates to a coating powder and method for its production. Said powder can be used in many technical fields, especially in machine and vehicle construction in chemical and petro-chemical installations. This coating powder has a hardmetal microstructure and consists of two cubic hard material phases, which respectively constitute a core-rim structure of a hard material particle. The hard material phase in the core contains Ti and C and the hard material phase in the rim contains Ti, a second metal and C, and these are embedded in a binder phase containing one or more of the elements Ni, Co and Fe. According to the invention, said coating powder is characterized by the fact that at least one additional alloying element exists either in the hard material phase, in the binder phase or in both phases simultaneously. According to the invention, the coating powder is produced by mixing and homogenizing the individual hard materials and the metal powder in an aqueous suspension in a ball type mill, which are later on granulated, sintered and processed using a grinding technique.



ABSTRACT

The invention relates to a coating powder and method for its production. Said powder can be used in many technical fields, especially in machine and vehicle construction in chemical and petro-chemical installations. This coating powder has a hardmetal microstructure and consists of two cubic hard material phases, which respectively constitute a core-rim structure of a hard material particle. The hard material phase in the core contains Ti and C and the hard material phase in the rim contains Ti, a second metal and C, and these are embedded in a binder phase containing one or more of the elements Ni, Co and Fe. According to the invention, said coating powder is characterized by the fact that at least one additional alloying element exists either in the hard material phase, in the binder phase or in both phases simultaneously.

According to the invention, the coating powder is produced by mixing and homogenizing the individual hard materials and the metal powder in an aqueous suspension in a ball type mill, which are later on granulated, sintered and processed using a grinding technique.

COATING POWDER AND METHOD FOR PREPARATION THEREOF

Field of the Invention

The invention concerns a coating powder for use in different coating technologies such as the different variants of thermal spraying, for example, plasma spray, high velocity oxy-fuel spraying (HVOF) and detonation spray, the same as other methods like coating by means of laser or plasma transferred arc (PTA) welding. By means of said methods the coating powder according to the invention can be applied to different highly stressed construction units which are exposed to the most varied stresses such as abrasive and erosive wear, corrosion and high temperatures, or to the most varied combinations of said stresses, being used in the most diverse technical fields. Examples of use are coated construction units in vehicles and machinery construction, chemical and petrochemical installations and many other branches of the economy.

Related Art

Different hardmetal-like coating powders are widely used in technology. They are characterized by a carbide hard material such as WC or Cr_3C_2 embedded in a ductile binder matrix. The most important systems for coatings are WC-Co and Cr_3C_2 -NiCr. WC-Co shows a very high resistance to wear. The use at elevated temperature (up to a maximum of 450°C) and simultaneous chemical strain is limited. It has been sought by using other binders like Ni and alloys with chromium specially to improve the resistance to corrosion which due to the low alloying property of the system is only limitedly possible. On the other hand, Cr_3C_2 -NiCr can be satisfactorily used at high temperatures (up to $750\text{-}800^\circ\text{C}$) and corrosive strain. But the resistance to wear of the system is lower than that of WC-Co.

Because of their great hardness, low density and good availability, there have been repeatedly undertaken in the past tests for developing a

- 1 hardmetal-like powdery coating material on a base of cubic Ti hard material
- 2 phases [TiC or Ti(C,N)⁷] from which coatings not having the above mentioned

1 disadvantages can be produced using current coating technologies, specially
2 technologies associated with the process group of thermal spray, for example,
3 plasma spray, high-velocity oxy-fuel spraying (HVOF) and detonation spray,
4 the same as other methods such as coating by means of laser or plasma
5 transferred arc (PTA) welding.

6 In DD 224 057 has been described a coating powder having a base of
7 TiC which together with at least one of the metals Ni, Co, Cr, W as well as B
8 and/or Si, also contains Mo or Mo₂C and free carbon. Individual components
9 such as Mo₂C can here be bonded on the TiC. Due to the fact that there
10 exists no composite powder having a hardmetal-like microstructure and the
11 individual powder components are very coarse, no coatings very resistant to
12 wear can be produced.

13 In DE 41 34 144 has been described a carbide spray powder where by
14 coating with an active carbon the core should be protected against oxidation
15 phenomena. As spray powders to be coated, there are mentioned, also
16 titanium carbide and titanium carbonitride, in a matrix of metals of the
17 group iron, nickel and cobalt.

18 Several patents describe methods for preparing hardmetal-like
19 coatings with TiC as hard material phase or coated construction parts. WO
20 87/04732 describes a method for preparing a wear-resistant coating from a
21 powder material which contains 10-50% by weight TiC and a Fe and/or Ni
22 alloy, or a Co alloy. In these compositions the portion of the hard material
23 phase is too low for decisively increasing the wear resistance.

24 U.S. Patent 4,233,072 uses for coating piston rings mechanical
25 mixtures of the composition 60-85% Mo, 10-30% of a NiCr alloy and 5-20%
26 TiC. Together with the disadvantages due to the mechanical mixture, the
27 hard material portion is also exceedingly low.

1 S. Economou et al (Wear, Vol. 185, 1995, pp. 93-110) describe several
2 alloy variants of hardmetal-like coating powders with TiC, TaC or (Ti,Ta)C as
3 hard material phase as well as NiCrMo or Mo as binder phases. The portion
4 of the carbide hard materials was 60% vol. Said coating powder was
5 prepared from the existing individual hard materials, a NiCr alloy powder
6 and metallic molybdenum by agglomeration (interpreting SEM photographs
7 a spray drying process must be assumed here) and sintering at 1200°C/6h
8 under argon. From X-ray investigations for the highest alloyed (Ti,Ta)C-
9 NiCrMo coating powder it results that after sintering molybdenum was still
10 detectable as phase. Therefore, the green density of the spray-dried,
11 granulated material and/or the sintering temperature were too low
12 completely to dissolve the molybdenum with the other components of the
13 binder phase or to form a Mo-containing hard material phase. The grain size
14 range of said coating was 25-90 µm or 20-75µm. Nevertheless, comparing
15 with one another the tested coating systems, the best coatings were obtained
16 with the alloy variant (Ti,Ta)C-NiCrMo. Coatings using only TiC as hard
17 material phase showed poor wear-resistant properties.

18 EP 0 425 464 describes a roller for use in the production of paper
19 which is provided with several coatings. The surface coating constitutes a
20 hardmetal-like coating, the hard material phase of which consists of
21 tungsten, chromium, titanium, niobium or boron carbides or a mixture
22 thereof and the metal binder phase of which consists of Ni, Co or Fe or alloys
23 thereof, which can also be alloyed with transition metals of the IV to VI
24 cosets of the PTE. The content of the hard material phase can amount up to
25 96%. Due to the insufficient microstructural formation in the coating
26 powder, the substrates coated therewith show poor wear characteristic so
27 that the field of use of such a coating remains limited to said special case.

1 M. Yu. Zashlyapin et al. (Sashchitnye pokytiya na metallakh, Vol. 20,
2 1986, pp. 52-55) describe coating powders having TiCN as hard material phase
3 and binders consisting of 75% by weight Ni and 25% by weight Mo which are
4 contained in the composite powder at 35-65% by weight. This corresponds to
5 65-78% by volume of hard material phase in the coating powder. According to
6 the results of the X-ray analyses, the sintered spray powders consist of TiCN
7 and a solid solution of TiCN and Mo in the nickel matrix. Due to the use of Mo
8 as starting material and the small content of non-metals combined therewith,
9 this powder is susceptible to oxidation and the substrates coating therewith
10 show poor wear characteristic.

11 P. Vuoristo et al. (TS'96: Oral and poster presentations of the Thermal
12 Spray Conference '96, March 6-8, 1996, Essen, publisher: E. Lugscheider,
13 DVS Reports, Vol. 175, Düsseldorf, Deutscher Verlag für Schweißtechnik,
14 1996, pp. 58-60) describe coating powders with (Ti, Mo)C as hard material
15 phase and NiCo in the binder phase. The content of carbide hard materials in
16 the coating powders amounted to 72 by vol. or 80% by vol. Said materials
17 show core-rim structures of the hard material phases, the hard material phase in
18 the core being a TiC and that in the rim a (Ti,Mo)C_{1-x}. The content of
19 molybdenum is not specified. Although the coatings produced from said
20 coating powders are better than those produced from TiC containing coating
21 powders of the prior art, still they are not so decisively improved (for example
22 abrasive wear) as to be sufficiently superior and competitive in comparison
23 with other hardmetal systems.

24 Summary of the Invention

25 The problem to be now solved by this invention is to make possible to
26 propose a coating powder on the base of cubic hard material phases with
27 titanium as metal main component which by alloying techniques are easy to
28 carry out so that the coating powders described in the prior art are decidedly
29

1 improved and so that with current coating technologies coatings can be
2 produced that are competitive or superior to the other hardmetal systems.

3 With this hardmetal-like coating powder proposed by the invention, it
4 becomes possible to produce by conventional coating technologies highly
5 stressed construction parts with hardmetal-like, extremely resistant coatings
6 which compared to the known technical solutions have improved
7 combinations of properties like high resistance to wear at high temperature,
8 high resistance to wear at simultaneous highly corrosive strains, lower
9 coefficients of friction at high temperature and which by varying the
10 composition can be easily adapted to different stress profiles.

11 A problem to be solved by the invention at the same time is to indicate
12 an economical method for preparing said spray powder.

13 In conformity with the invention these problems concerning the
14 coating powder are solved according to one or more of Claims 1 to 18 and
15 concerning the method of preparation of said powder, according to one or
16 more of Claims 19 to 21.

17 The coating powder according to the invention is characterized by
18 having a hardmetal-like microstructure. Here at least two cubic hard
19 material phases which have a core-rim structure and form a hard material
20 grain are embedded in a metal binder matrix consisting of at least one or
21 more of the elements Ni, Co and Fe. Said core-rim structure is formed by
22 metallurgical reactions, solution and reprecipitation phenomena in the
23 sintering process during the preparation of the coating powder. The function
24 of the hard material phase in the rim is to improve in particular the deficient
25 wetting of the pure hard material TiC with the usual binder metals Ni, Co
26 and Fe or alloys thereof. Specially adequate for this have proved to be the
27 metals Mo and W which specially in the form of the carbides thereof Mo₂C or

1 WC are admixed as starting powders in the preparation of the coating
2 powder. During the sintering process said carbides dissolve relative to the
3 TiC preferably in the binder and in the cooling phase of the sintering process
4 reprecipitate as mixed carbides (Ti,Mo)C_{1-x} or (Ti,W)C_{1-x} in the form of rims
5 around undissolved TiC grains. Thus, in the coating powder compositions
6 [for example (Ti, Mo)C-NiCo] and structures are formed as have already been
7 described by P. Vuoristo et al (TS'96): Oral and poster presentations of the
8 Thermal Spray Conference '96, March 6-8, 1996, Essen, publisher: E.
9 Lugscheider, DVS reports, Vol. 175, Düsseldorf, Deutscher Verlag für
10 Schweisstechnik, 1996, pp. 58-60), as above explained in detail in the prior
11 art. In metallographically prepared cross-sections of the coating powders the
12 microstructures thereof are to a large extent identical to the microstructures
13 of sintering bodies of analogous composition produced by powder metallurgy.
14 But it has been found that such alloying degree (two-phase, cubic hard
15 material particles with core-rim structure in a binder matrix of at least one
16 or more of the elements Ni, Co and Fe) as the rule is insufficient for
17 industrial uses and according to the invention said deficiency can be
18 overcome by adding at least one other alloying element.

19 Nitrogen is advantageously added as one other alloying element. This
20 is obtained by partly or wholly substituting titanium carbide by titanium
21 carbonitride used as starting material for preparing the coating powder.
22 From developments for cutting tools, it is known that by increasing the
23 content of nitrogen, specially the Mo and/or W contents can be increased in
24 the binder phase (P. Ettmayer et al., Int. J. Refractory Metals & Hard
25 Materials, 1995, No. 6, Vol. 13, pp. 343-351). Due to the known fact that
26 from carbonitrides at high temperatures such as appear in the thermal spray
27 process nitrogen is set free, the use of nitrogen in a commercial hardmetal-

1 like coating powder has to date been avoided. But it has been shown that by
2 the microstructural formation of the coating powder according to the
3 invention, the hard material phases are protected against nitrogen losses in
4 the spraying process. The use of nitrogen-containing coating powders is
5 specially advantageous when coatings with a low friction coefficient have to
6 be produced. The elements Zr, Hf, V, Nb, Ta and Cr are also additional
7 alloying elements according to the invention. They can be used both alone
8 and together with nitrogen. Alloying elements such as Al, B and others are
9 likewise advantageous in particular applications.

10 It is of special advantage to introduce for the preparation of the
11 coating powders metal alloying elements in the form of carbides. This applies
12 to the alloying elements Mo and W as well as to the other metal alloying
13 elements Zr, Hf, V, Nb, Ta and Cr and both to nitrogen-free and to nitrogen-
14 containing compositions of the coating powders according to the invention.
15 This can result in that after the sintering process, together with cubic hard
16 material phases forming the core-rim structure there can be detected other
17 separately existing also non-cubic hard material phases. This occurs when
18 there are exceeded the solution limits for said hard materials in the cubic
19 hard material phases which form the core-rim structure. Cr_3C_2 , Cr_7C_3 ,
20 Cr_{23}C_6 , WC, W_2C and Mo_2C can still be detected after the sintering process
21 by X-ray diffraction analysis. For example, the orthorhombic Cr_3Cr_2 is still
22 detectable after sintering by X-ray diffraction analysis when used in a certain
23 amount. Many coating processes such as the plasma spray in air, the high
24 velocity oxy-fuel spraying and the detonation spray lead to partial oxidation
25 of hardmetal-like coating powders. It is known that the carbide hard
26 materials Cr_3C_2 , Cr_7C_3 , Cr_{23}C_6 , WC, W_2C and Mo_2C oxidize under formation
27 of free carbon and a lower carbide of the metal – when it is stable – and then

1 the metal itself is formed (R.F. Voitovich, Okislenie karbidov i nitridov, Kiev,
2 Naukova dumka, 1981). This metal, which is formed, is capable further to
3 alloy the metal binder. Thus, it is at the same time obtained that the alloying
4 state of the binder is positively affected and that the oxygen content of the
5 coating is reduced. The chromium which is formed by oxidation of the Cr_3Cr_2
6 considerably increases the resistance to corrosion of the binder. It is at the
7 same time important that all carbide and carbonitride starting materials
8 used for the preparation of coating powders have a low oxygen content.

9 When using individual hard materials for the preparation of coating
10 powders such as TiC , Ti(C,N) , Mo_2C or WC , with the exception of Ti , there
11 are practically no other metals like Mo , W , Ta and Nb in the hard material
12 phase forming the core. Together with the individual hard materials there
13 can also be used pre-formed carbides and carbonitrides such as $(\text{Ti}, \text{Mo})\text{C}$,
14 $(\text{Ti}, \text{W})\text{C}$ or $(\text{Ti}, \text{W})(\text{C}, \text{N})$. The consequence of such a procedure is that, as
15 known from the development of cutting tools (P. Ettmayer et al., Int. J.
16 Refractory Metals & Hard Materials, 1995, No. 6, Vol. 13, pp. 343-351), the
17 hard material phase present in the core contains together with titanium
18 other metals. Such a distribution of the alloying elements is likewise in
19 accordance with the present invention. To the special extent this concerns
20 also the use of Ti(C,N) as starting material. It is known that in the core of
21 the hard material particles an increased concentration of the nitrogen results
22 while in the rims the nitrogen content is small, but an increased
23 concentration of Mo or W is observed (P. Ettmayer, H. Kolaska, Metall, 1989,
24 Vol. 43, Number 8, pp. 742-749). According to the invention this means that
25 the content of titanium and carbon in the cores of the hard materials
26 amounts to >60 atom%, and at the same time in the rim the content of
27 titanium, of the second metal and carbon amounts to >50 atom%. As a rule

1 real values are clearly above the indicated limit values. In special alloying
2 variants several rim phases can also be detected.

3 In principle, the volume ratio between the hard material phases and
4 the binder phase can be varied within wide limits in the coating powder
5 according to the invention, but a sufficiently high resistance to wear of the
6 coatings is obtained only when the volume portion of the hard materials
7 related to the starting materials prior to sintering amounts to >60% vol.

8 For preparing the coating powders according to the invention there can
9 be used individual hard materials like TiC, TiN, Ti(C,N), Mo₂C, WC and
10 Cr₃C₂ and also complex hard materials like (Ti,Mo)C and (W,Ti)C. But
11 individual hard materials are preferably used. The carbon content of the
12 titanium-containing hard materials is in the range of 4 to 21% by weight, the
13 nitrogen content amounts to a maximum of 17% by weight. When using TiC
14 or Ti(C,N), this corresponds to all compositions of the solid solution of TiC
15 substantially up to TiC_{0.3}N_{0.7}. In the corresponding ratio, TiC and TiN can
16 also be used as starting materials. Related to the starting materials prior to
17 sintering and to the total hard material portion of the coating powders when
18 using the individual hard materials TiC, TiN or Ti(C,N), the volume portion
19 of said titanium-containing hard materials amounts to 50-95% vol.,
20 preferably 60-85% vol. In case of using a third hard material phase, the
21 portion thereof amounts to a maximum of 35% vol., preferably a maximum of
22 25% vol. The portion of the second hard material phase responsible for the
23 formation of the core-rim structure results from the difference.

24 The alloying elements such as W, Mo, Cr are preferably added as
25 carbides and can dissolve during the sintering process in the preparation of
26 coating powder both in the cubic hard material phases and partly in the
27 binder phase.

1 The core-rim structure of the cubic hard material phases which is
2 characteristic for the coating powder is transferred into the coating and is
3 detectable therein. Another advantage of the coating powders according to
4 the invention is that they can be processed to coatings nearly equal with the
5 most different process variants of thermal spray technology.

6 With the solution according to the invention, it has been accomplished
7 to prepare coating powders on the base of the hard material TiC by means of
8 which coatings that are competitive or superior to the other hardmetal
9 systems can be produced by current coating technologies, specially the
10 technologies associated with the process group of the thermal spraying, for
11 example, plasma spray, high velocity oxy-fuel spraying (HVOF) and
12 detonation spray, as well as with other processes like coating by means of
13 laser or plasma transferred arc (PTA) welding. Despite of all the efforts up to
14 this date, this was impossible according to the prior art and has resulted in
15 prejudices in the technical world in a manner such that it has been said, for
16 example, that "TiC has only little importance on account of its inclination to
17 oxidation and the resulting coating properties therefrom which can be
18 overcome only by considerable precautions" (J. Beczkowiak et al., Schweissen
19 and Schneiden, (Welding and Cutting), 1996, Vol. 58, Number 2, pp. 132-
20 136).

21 The coating powder according to the invention can be produced by
22 different technologies for coating powder production which include as most
23 important technological step a sintering process, for example, like sintering
24 and crushing. But with the technology of sintering and crushing the coating
25 powder particles produced are of irregular morphology. For processing
26 coating powders it has been found that a spherical morphology which
27 increases the flowability of the powder is specially effective. Therefore,

1 agglomeration and sintering have been used as preferred technology for
2 preparing the spraying powders according to the invention. A spray drying
3 process is advantageously used for agglomeration. The spray drying
4 parameters are to be selected so as to obtain granules of high green density
5 which are densified by a simple sintering process in which the core-rim
6 structure of the hard material phases in the binder matrix can be formed. The
7 high green density of the spray drying granules is also important in a manner
8 that the sintering between individual granules remains limited to a minimum.
9 The sintering process leads to a change in the phase composition of the coating
10 powders due to the metallurgical reactions, solution, and reprecipitation
11 reactions, the changes of the elementary composition are negligible. The size
12 of the core-rim structured hard material particles in the sintered coating powder
13 amounts to $<10\mu\text{m}$, but preferably to $<5\mu\text{m}$. After sintering, the lightly
14 agglomerated by sintering of individual granules coating powder is finished by
15 a careful milling process and then, for its use, according to the requirements, in
16 one of the coating technologies mentioned, fractionized.

17 The grain size of the coating powder according to the invention must be
18 adapted to the requirements of the coating technology used, wherefore it can be
19 within a wide range of $10\text{-}250\mu\text{m}$.

20 21 Brief Description of the Drawings

22 The invention is explained hereby by several examples in connection
23 with the drawings, where:

24 Fig. 1 illustrates a metallographic cross-section of a coating powder
25 particle 3,000 times enlarged;

26 Fig. 2 illustrates a metallographic cross-section through several particles
27 of the coating powder 700 times enlarged;

28 Fig. 3 shows the microstructure of one coating powder particle enlarged
29 8000 times; and

1 Fig. 4 shows the morphology of the spraying powder according to the
2 invention.

3

4 Example 1

5 59.6% wt. $\text{TiC}_{0.7}\text{N}_{0.3}$, 12% wt. Mo_2C and 28.4% wt. Ni corresponding to
6 80.4% vol. hard material portion and 19.6% vol. binder portion are premixed
7 dry, dispersed in water and then intimately mixed in a ball mill in high-grade
8 steel containers with hardmetal balls. To the suspension is added 1.5%

1 wt. of an adapted binder of polyvinyl alcohol and polyethylene glycol and
2 then granules of spherical shape are produced by spray drying. The binder is
3 removed together with the sintering in a one-step annealing operation. The
4 binder removal and annealing are carried out in flat graphite crucibles under
5 argon at a heating rate of 5 K/min up to 600°C and 10 K/min up to the
6 sintering temperature of 1320°C followed by an isothermal treatment of 30
7 min. Figure 1 shows the metallographic cross-section of a coating powder
8 particle 3000 times enlarged. The core-rim structure of the hard material
9 particles is clearly to be detected. The sintered powders are subjected to a
10 careful milling and thereafter, depending on requirements, fractionated for
11 use in the different coating technologies. For use in the high velocity oxy-fuel
12 spraying or detonation spraying, the preferred grain size amounts to 20-
13 45µm. The d10 in this powder corresponds to 20 µm, the d90 to 42 µm.

14 The powder with the grain size of 20-45 µm was processed with a
15 detonation spray equipment "Perun P" (Paton Institut, Ukraine) with a
16 barrel having a length of 660 mm and 21 mm diameter to form coatings
17 having a thickness of approximately 250 µm on steel substrates adequate for
18 the abrasion test. Here were used the spraying conditions optimized for this
19 material. The spraying distance was 120 mm with a firing rate of 6.6
20 detonations/s. An acetylene/oxygen mixture in the volume ratio of 1.0 was
21 used. These coatings were subjected to an abrasion wear test according to
22 U.S. standard ASTM G 65-85 without corrosive strain. The weight loss after
23 5904 m wear length amounted to 110 mg. For comparison with standard
24 materials, in view of the density difference, this must be converted to mm³
25 and amounted to 16.5 mm³. In tests with the standard materials WC-12%Co
26 and Cr₃C₂-25%NiCr, the amount of volume losses corresponds to 7.0 mm³ and
27 15.9 mm³. These materials were sprayed with the parameters optimal for

1 them, that is, the volume ratio of the acetylene/oxygen mixture amounted to
2 1.3.

3 Example 2

4 From 59.6% wt TiC, 12.0% wt. Mo₂C, 8.5% wt. Cr₃C₂ and 19.9% wt. Ni
5 and corresponding therewith 86.8% vol. hard material portion and 13.2% vol.
6 binder portion, a coating powder was prepared following the same procedure
7 as in Example 1. Differences resulted in the sintering temperature which
8 here amounted to 1300°C. Figure 2 shows the metallographic cross-section
9 through several particles of the coating powder 700 times enlarged. The
10 microstructure of one of said coating powder particles is shown in Figure 3
11 enlarged 8000 times. The portion of the light binder phase is substantially
12 less than in the coating powder of Example 1. Together with hard material
13 particles having a core-rim structure, particles of a third carbide hard
14 material phase are observed. The coating powder was fractionated, for
15 spraying tests there was also used a grain size range of 20-45µm. The
16 morphology of said spraying powder according to the invention is shown in
17 Figure 4. The coating powder was processed under spraying conditions
18 similar to Example 1 with the detonation spraying equipment "Perun P"
19 (Paton Institut, Ukraine), also to form coatings with a thickness of
20 approximately 250 µm on steel substrates adequate for the abrasion test.
21 The weight loss after 5904 m wear length amounted to 68 mg, when
22 converted to the volume loss 10.6 mm³.

23 Example 3

24 From 59.6% wt TiC_{0.7}N_{0.3}, 12.0% wt. Mo₂C, 8.5% wt Cr₃C₂ and 19.9%
25 wt Ni and corresponding therewith 86.5% vol. hard material portion and
26 13.5% vol. binder portion, a coating powder was produced following the same
27 procedure of Example 1. Differences resulted in the sintering temperature

1 which here amounted to 1300°C. The microstructure of this coating powder
2 corresponds to that of Example 2. The coating powder was fractionated, for
3 spraying tests there were likewise used grain sizes of 20-45µm. The coating
4 powder was processed under spraying conditions similar to those of Example
5 1 with the detonation spraying equipment "Perun P" (Paton Institut,
6 Ukraine) also to form coatings having a thickness of approximately 250 µm
7 on steel substrates adequate for the abrasion test. The weight loss after 5904
8 m wear length amounted to 58 mg, when converted to the volume loss 8.9
9 mm³.

10 Example 4

11 From 56.5% wt. TiC, 12.0% wt Mo₂C, 3.0% wt NbC and 28.5% wt Ni
12 and corresponding therewith 80.4% vol hard material portion and 19.6% vol.
13 binder portion, a coating powder was prepared following the same procedure
14 as in Example 1. Differences resulted in the sintering temperature which
15 amounted here to 1300°C. The microstructure of said coating powder
16 corresponds to that in Example 2. The coating powder was fractionated, for
17 spraying tests there were also used grain sizes of 20-45µm. The coating
18 powder was processed under spraying conditions similar to Example 1 with
19 the detonation spraying equipment "Perun P" (Paton Institut, Ukraine) also
20 to form coatings with a thickness of approximately 250 µm on steel
21 substrates adequate for the abrasion test. The weight loss after 5904 wear
22 length amounted to 80 mg, when converted to the volume loss 12.1 mm³.

23 Example 5

24 A coating powder from Example 1 was sprayed with a PT A-3000S
25 plasma spraying equipment with a F4 torch in air also on steel substrates
26 adequate for the abrasion test. For this purpose was used an Ar/H₂-plasma
27 (best results at 45 l/min Ar and 14 l/min H₂) with a plasma power of 38 kW.

1 The weight loss after 5904 wear length amounted to 100 mg when converted
2 to the volume loss 16.4 mm³.

3 For coatings of the standard materials WC-12%Co and Cr₃C₂-25%
4 NiCr sprayed with the same equipment the amount of volume losses
5 corresponded to 10.8 mm³ and 20.3 mm³, respectively. These materials were
6 sprayed with the optimum parameters for them, that is, using an Ar/He
7 plasma (Ar: 60 l/min, He 120 l/min, 44 kW plasma power, 110 mm spraying
8 distance).

9 Example 6

10 A coating powder from Example 1 was sprayed by high velocity oxy-
11 fuel spraying with a PT CDS spraying equipment with a gaseous mixture of
12 hydrogen (600 l/min) and oxygen (300 l/min) with a spraying distance of 200
13 mm likewise on steel substrates adequate for the abrasion test. The weight
14 loss after 5904 wear length amounted to 94 mg, when converted to the
15 volume loss 15.4 mm³.

What is claimed is:

1. Coating powder having a hardmetal microstructure consisting of two cubic hard material phases which respectively constitute a core-rim structure of hard material particles wherein the hard material phase in the cores contains Ti and C and the hard material phase in the rims contains Ti, a second metal and C and these are embedded in a binder phase consisting of one or more of the elements Ni, Co and Fe, wherein either in the first and second hard material phases or in the binder phase, or in both simultaneously one or more alloying elements is present, and in the metal binder phase optionally is embedded one or more additional carbide hard material phases which during spraying processes under oxygen-containing atmosphere decomposes with carbon loss and the metal component thereof alloys the first and second hard material phases and/or the binder phase, or remains dissolved in the binder as carbide due to cooling.
2. Coating powder according to claim 1, wherein the cubic hard material phase in the rims contains as said second metal Mo or W.
3. Coating powder according to claim 1, wherein the alloying element is N and/or one or more elements selected from the group consisting of Zr, Hf, V, Nb, Ta and Cr.
4. Coating powder according to claim 1, wherein the metal binder phase is additionally alloyed by W and/or Mo, but one or both elements are simultaneously contained in the cubic hard material phase that forms the rims.
5. Coating powder according to claim 1, wherein each additional added carbide phase has a cubic or other crystal lattice.
6. Coating powder according to claim 1, wherein the carbide phases are Cr_3C_2 , Cr_7C_3 , Cr_{23}C_6 , WC, W_2C and Mo_2C .
7. Coating powder according to claim 1, wherein the volume portion of the total of the hard materials related to the total volume of the materials prior to the sintering amounts to >60% vol.
8. Coating powder according to claim 7, wherein the volume portion of the hard materials related to the total volume of the materials prior to sintering is within the 70-95% vol. range.

9. Coating powder according to claim 8, wherein the volume portion of the hard materials related to the total volume of the materials prior to sintering is within the 80-95% vol. range.

10. Coating powder according to claim 1, wherein related to the total of the materials prior to sintering, the titanium-containing hard materials have up to 4-22% wt carbon content.

11. Coating powder according to claim 7, wherein the volume portion of the titanium-containing hard materials when using the individual hard materials TiC, TiN or Ti(C, N) amounts to 50-95% vol. related to the total volume of the materials prior to sintering and to the total portion of hard materials.

12. Coating powder according to claim 11, wherein the volume portion of the titanium-containing hard materials when using the individual hard materials TiC, TiN or Ti(C, N) amounts to 60-90% vol. related to the total volume of the materials prior to sintering and to the total portion of hard materials.

13. Coating powder according to claim 1, wherein the volume portion of the additional carbide hard material phase amounts to a maximum of 35% vol. related to the total volume of the materials prior to sintering and to the total portion of hard material.

14. Coating powder according to claim 13, wherein the volume portion of the additional carbide hard material phase amounts to a maximum of 25% vol related to the total volume of the materials prior to sintering and to the total portion of hard materials.

15. Coating powder according to claim 1, wherein the grain size of the particles following sintering is within the range of 10-250 μm .

16. Coating powder according to claim 15, wherein the grain size of the particles following sintering is within the range of 20-90 μm .

17. Coating powder according to claim 16, wherein the grain size of the particles following sintering is within the range of 20-45 μm .

18. Coating powder according to claim 15, wherein the particles following sintering have a spherical morphology.

19. Process for the preparation of the coating powder according to claim 1, wherein the hard material particles are mixed and homogenized in an aqueous suspension by mixed

grinding in a ball-type mill and then granulated, sintered and prepared using a grinding technique.

20. Process for the preparation of the coating powder according to claim 19, wherein the granulation is carried out by spray drying.

21. Process for the preparation of the coating powder according to claim 19, wherein the sintering is carried out depending on the alloy composition at temperatures at which an effective amount of liquid phase is formed, which makes possible the metallurgic reactions, solution, and re-precipitation reactions needed to form therefrom the core-rim structure of the cubic hard material phases.

22. Coating powder according to claim 1, wherein related to the total of the materials prior to sintering, the titanium containing hard materials comprise TiN or Ti(C,N) having up to 17% wt nitrogen content.

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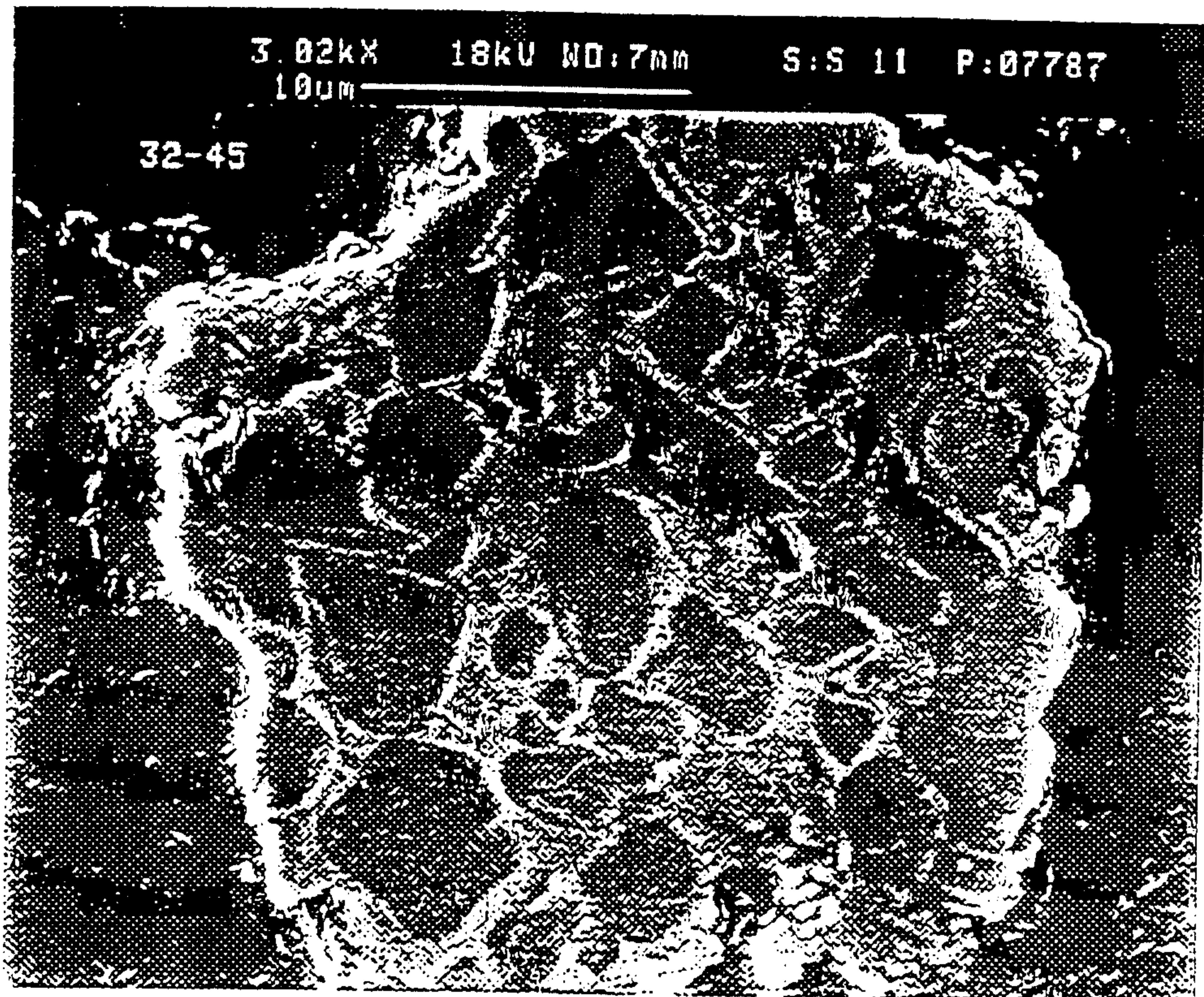


Fig. 1. 3000x enlargement of the metallographic cross-section of a particle of a coating powder according to Example 1

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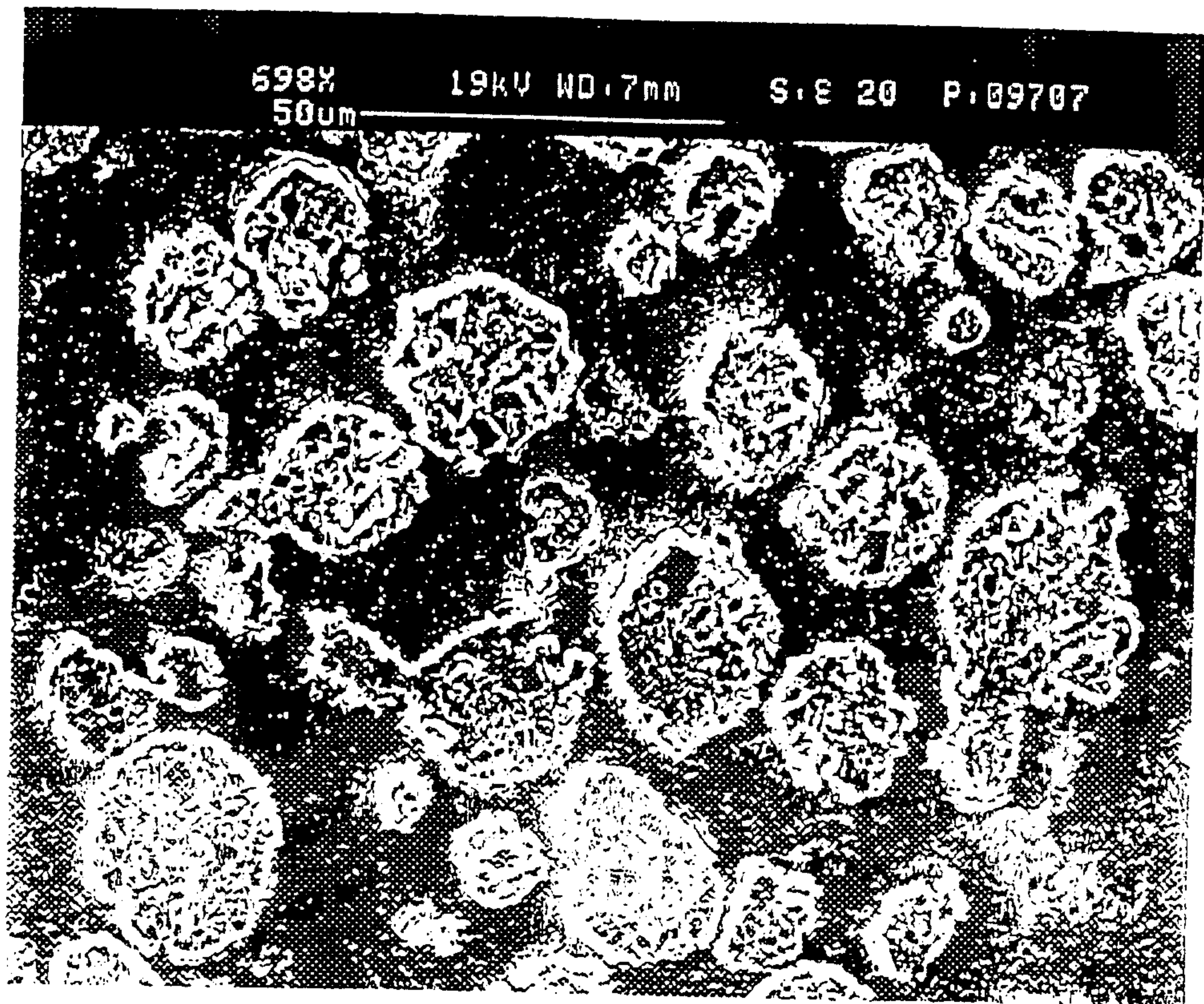


Fig. 2. 700x enlargement of metallographic cross-section of a number of a number of particles of the coating powder of Example 2

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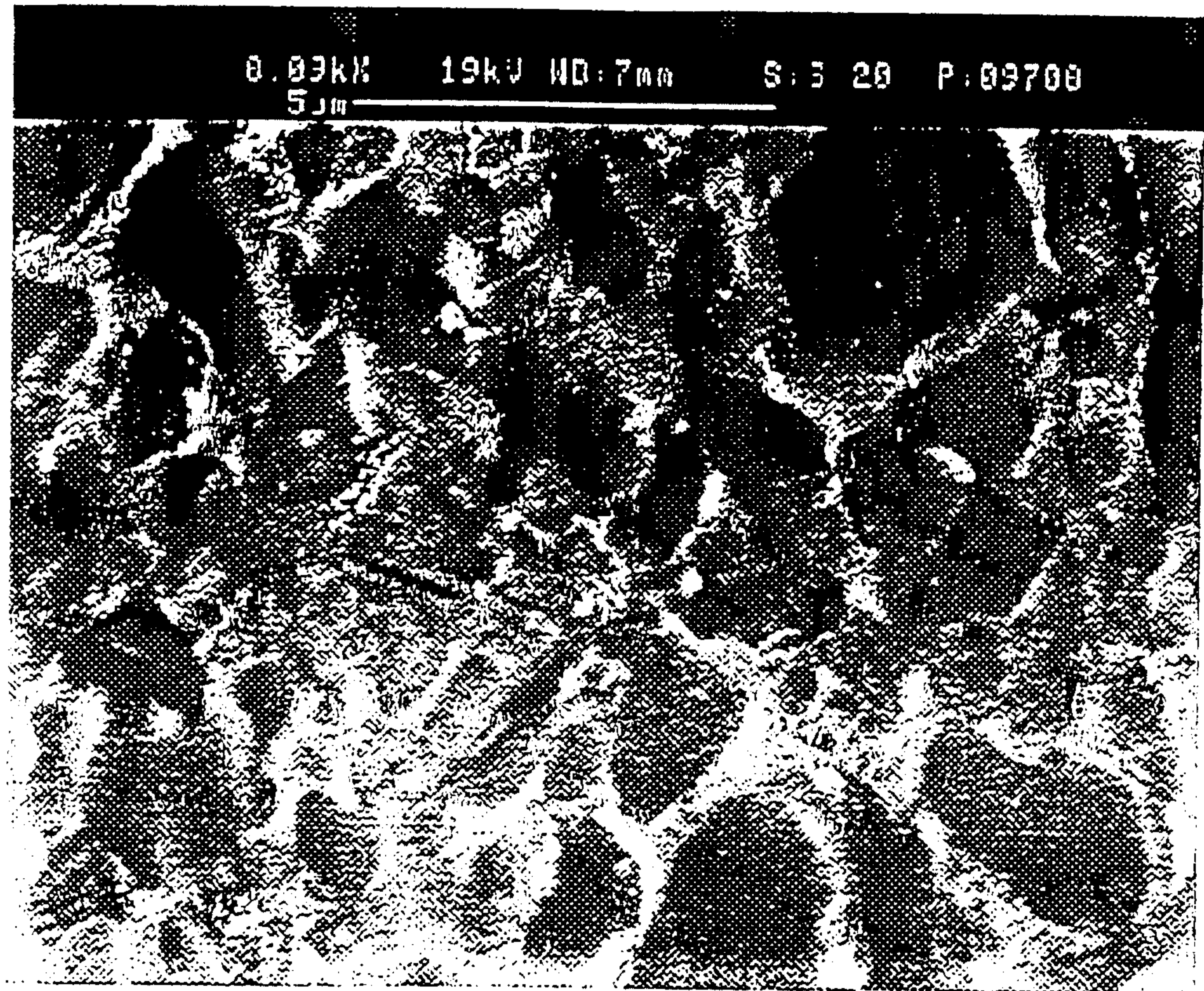


Fig. 3. 8000x enlargement of metallographic cross-section of a particle of the coating powder according to Example 2

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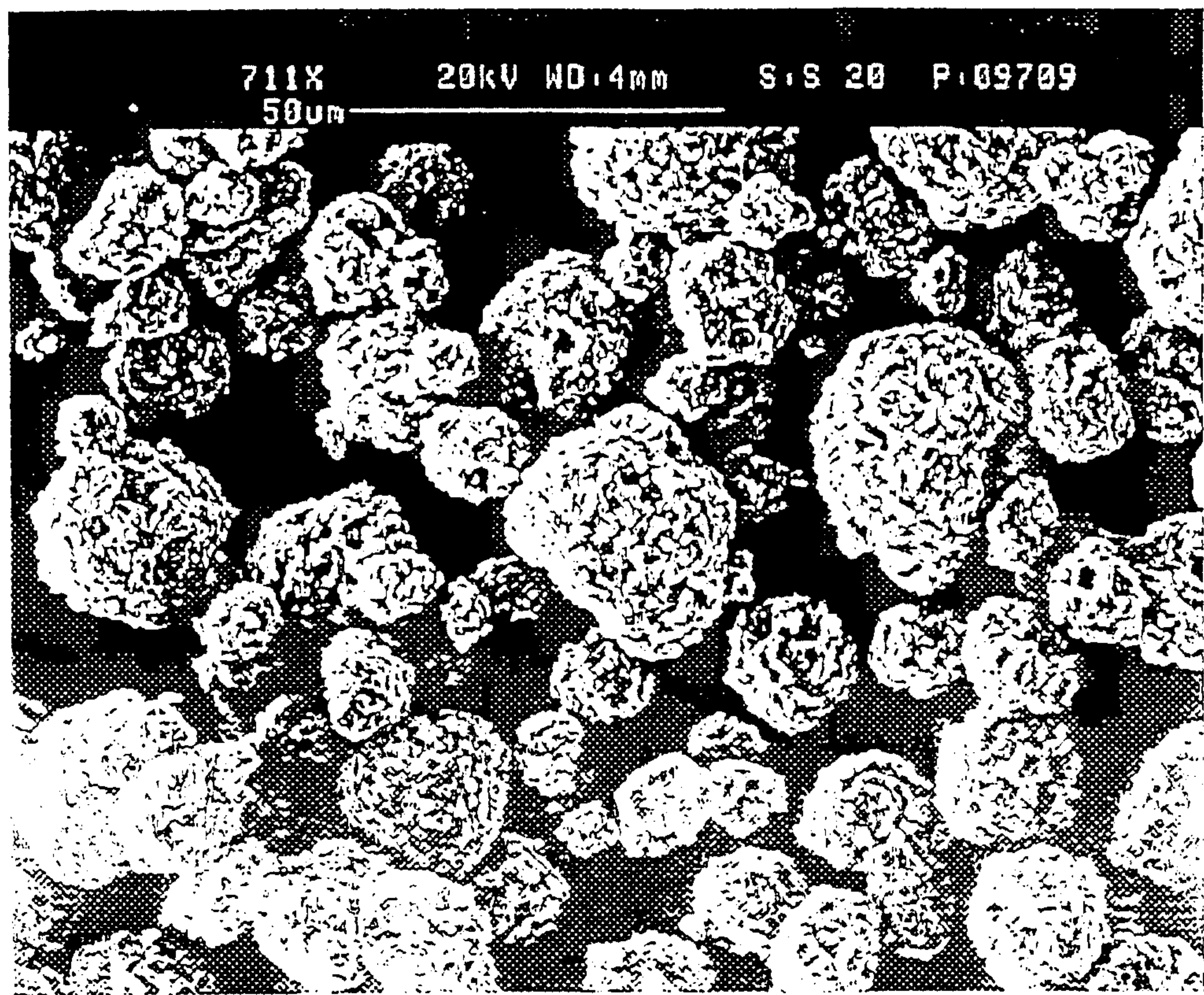


Fig. 4. The morphology of the coating powder according to Example 2 (700x enlargement)

711X

20kV WD:4mm

S.S 20

P:09709

50um



The morphology of the coating powder according to Example 2 (700x enlargement)