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Declarations under Rule 4.17:

- as to the identity of the inventor (Rule 4.17(i))
- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- of inventorship (Rule 4.17(iv))

(54) Title: METHOD FOR SINTERING A METAL WITH A PLASTIC MATERIAL

(57) Abstract: The invention relates to a method for sintering a metal with a plastic material in which the metal or metal alloy input material or alloys of their alloys or plastics or their modifications disintegrate as a result of pyrolysis on activated carbon and then compresses to the shape of the finished product. Then sintered, the temperature and sintering time being selected depending on the metal used to allow the particles to sinter and the sintering is carried out in a vacuum atmosphere or protective gas.



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Method for sintering a metal with a plastic material

The present invention relates to a method for the reactive sintering of a metal with a plastic material carried out in a vacuum atmosphere or a protective gas resulting in a porous material.

The closest known method to the proposed invention is the so-called "*Space holder method*", in which besides the metal powder, a second material (including plastics) is used to maintain the free space in the pressing process. In the next step, the additional material must be completely removed by pyrolysis, dissolved or otherwise removed. The resulting porous compact is then sintered. As a result, a porous metal sinter is obtained. The plastic used in this technique is completely disintegrated into gaseous particles by pyrolysis.

In the "reactive sintering" technique the plastic is intended not only to maintain the free space. During sintering, the pyrolysis of the plastic material with the release of active carbon occurs and the particles are deliberately released. These substances are pores, react with metal to form carbides and other compounds. As a result, a porous metal sinter with porosity is obtained in which the walls are covered with carbides and additional particles.

Control of the amount of plastic introduced, its type (plastic modification) and additional particles (particles introduced into the plastic prior to sintering in the process or to the metal mix at the mixing step) allow control of the surface reactivity of the sinter inside the sinter.

From the manufacturing point of view, the proposed technique is simpler than the Space holder technique. It is necessary to prepare the powder mixture then press and sinter without the additional time and laborious removal of the material that maintains the free space. From the point of view of the final product, the resulting material in the "reactive sintering" process is completely different from the product obtained by the "space holder" process. The "Space holder" method in a typical embodiment is GB714560 (A). Plastics that are completely

degraded by gas products during pyrolysis (such as polyolefins) are used. The advantage of this solution is that the plastic is completely removed and does not contaminate the sintered material. The difference is that in the solution of the invention plastic materials are used which, by pyrolysis, disintegrate into gaseous products and carbon particles. The resulting carbon particles are chemically active and react with the sintered metal to form a layer of carbides. With suitable sintering parameters, it will be possible to leave some of the active carbon inside the pores to allow for the creation of advanced materials such as chemically active filters (in this particular solution, the fiber particles in the form of fibers will be beneficial so as to provide controlled pore openness and the length of the path it will need. Medium to flow through the designed porous material).

The essence of the invention is a method of reactive sintering of a metal with a plastic in which the metal particle input material of their alloys or mixtures and plastics or their modifications disintegrate as a result of the pyrolysis of active carbon is firstly mixed to form a homogeneous mixture.

Then irons to the shape of the finished product. During ironing, the shape of the product is imparted, the advantage of this stage is that it is possible to compress under standard conditions using hydraulic presses at the processing temperature of the plastic used. The compactor obtained after pressing may have dimensions of the final product or larger for subsequent processing.

It is then sintered, the temperature and sintering time being selected depending on the metal used so as to allow the particles to sinter and the sintering is carried out under a vacuum atmosphere or protective gas. During sintering there is pyrolysis of plastic with the release of active carbon and other substances. The resulting reactive carbon reacts with the metal particles to form its carbides and penetrates into the metal structure. The pores formed inside the metal sinter have a controlled controlled reactivity depending on the materials used, sintering time and temperature.

If any of the input material particles is subject to change by contact with air, it is preferred that the mixing step is carried out in a protective atmosphere.

During ironing, it is envisaged to incorporate in the prepared mixture of metal or ceramic rods or fittings to enhance the strength and to impart the desired properties to the finished product. When using additional elements (rods, pipes), they should be precisely introduced into the compacts at the ironing stage.

65 In case the particles are to be inside the pipe, it will form a mold. It is also advantageous when the input material in the form of metal particles, their alloys or mixtures is in the form of grains, tiles or fibers in proportions consistent with the expected final sinter parameters. The process can use particles of both pure metals (all known), their alloys and mixtures. It is preferable to add modifiers or
70 additional particles of ceramics or chemical compounds in the form of grains, platens and fibers in the proportions necessary to achieve the desired sintered final parameters during the mixing step. The purpose of such treatments is to influence the sintering process (temperature expansion, gas emission, softening temperature, pyrolysis process, etc.) and final product properties (open / closed pores, oxides
75 and other compounds, introduction of special particles with special properties).

For special applications of the final product, it may be necessary to precisely position the particle type to ensure the required properties. In such a situation, these particles can be placed directly in the ironing form.

The advantage of the method of the invention is that it can utilize particles
80 of all known plastics and their modifications which pyrolysis produce active carbon particles and other solids such as, for example, polycarbonate. It is significant that the process is not suitable for plastics which, as a result of pyrolysis, are totally gasified (polyolefin).

The resulting sinter consists of the metal used, its carbides and additives
85 added to the sint intentionally or as a result of the chemical reaction of the substrates. The dimensions of the pores and their distribution within the sinter is closely related to the particle size (in grain, platelet, fiber) particle size used and the particle size (in the form of grains, tiles, fibers) of the sintered metal. The surface of the sinter and pores inside the material is enriched in carbon or metal-

90 coated carbide, particles introduced into the material prior to sintering and substances that are the products of the chemical reactions of the substrates.

The invention in the exemplary embodiment is shown in the drawing in which Fig. 1 is the XRD spectrum of the sinter surface after sintering of the titanium particle and PC polycarbonate particle; Figure 2 - SEM images of the sinter in four shots; Fig. 3 Measurement of microhardness of grinded surface of sinter and Fig. 4 Photo of Ti + PC sintered (20% by weight) using different size PC particles $\leq 200 \mu\text{m}$ a) $200 \div 400 \mu\text{m}$ b) $400 \div 630 \mu\text{m}$ c)

Method was performed to obtain Product containing titanium particles and Polycarbonate PC particles. Polycarbonate breaks down into active carbon and leaves the void in the final sinter with dimensions exactly as the particles have been applied. During the XRD study, only carbide TiC was identified in the outer layer. After sanding this layer, peaks from titanium, titanium carbide and titanium oxide appeared.

This material can be used as a biomaterial because TiC titanium carbide is biocompatible. Sintering of Ti (titanium) powder with PC Powder (polycarbonate).

In the protective atmosphere were mixed Ti 80% mass. and PC 20% mass. (~ 50/50 vol.) Then the prepared mixture weighing about 1g was compressed at 160 bar in a 8 mm diameter press. The prepared compact was sintered under vacuum at 1250 ° C (1h warm-up / 1h temperature / cooling with furnace).

After sintering, the compact is coated with a black layer of TiC carbide / active carbon. Dimensions of the moldings remain unchanged (not for samples with more PCs made in other tests - platelets have undergone plastics decay). After sanding the top layer, the surface of the pure Titan, the carburized area and the edges of the mold and the thin layer of carbide / active carbon inside the pores are exposed. The weight of the molded parts after sintering was reduced by about 10% compared to the weight of the moldings before sintering. The reason for this phenomenon is the escape of some of the PC pyrolysis reaction products in the form of gases. During the XRD analysis of the sinter surfaces (Figure 1), the

120 presence of TiC titanium carbide and various titanium oxide variants Ti_3O_5 , TiO_2
(R - Rutyl, B - Brukit) were identified. The presence of oxides is due to the
presence of a small amount of oxygen in the PC and the possible presence of
small amounts of oxygen in the sintering chamber. During the analysis of the
XRD spectra of the sinter after sanding the surface layer present in the spectrum
125 were also the peaks of the pure Titanium. The presence of Ti was also confirmed
in the EDS analysis during SEM scanning microscopy (Figure 2). During
hardness testing of the microhardness gauge (Figure 3), large deviations in the
hardness of the Titan between the pores were found. The hardness measured
ranged from 400 to 700 $\text{HV}_{0.03}$ depending on the measuring point and its distance
130 from the carved area of the pores.

Also, a direct correlation was found between the particle size of the PC
powder and the pore size in the finished sinter (Fig. 4).

Because the resulting material is different from the currently available
porous materials (porous metals or porous ceramics) with the possibility of
135 designing physicochemical activity of the interior of the pores and the possibility
of designing the distribution of pores in the final product (using scaffold, rods,
etc.), the invention may be applied. In various fields such as light constructions,
mechanical and acoustic damping, impact energy absorption, biomedical
(implants), filters (particle filters / chemically active filters), chemical active
140 devices (catalysts, reactors, sensors) (Tensile and conductive) or sensor
production.

Claims

1. Method of sintering metal with a plastic material, characterized in that the input material in the form of metal particles or their alloys or mixtures and plastics or their modifications disintegrating as a result of pyrolysis on activated carbon is mixed to a homogeneous mixture and then compressed to a finished shape, the product is then sintered, the temperature and sintering time being selected depending on the metal used to allow the particles to sinter and the sintering is carried out under a vacuum or protective gas atmosphere.
2. Method according to claim 1, characterized in that the mixing step is carried out in a protective atmosphere.
3. Method according to claim 1 or 2 characterized in that, during the pressing of the material, additional elements in the form of bars, metal or ceramic pipes are introduced into the prepared mixture.
4. Method of claim 1, 2 or 3, characterized in that the metal particle input material, their alloys or mixtures is in the form of grains, tiles or fibers in proportions consistent with the expected final sinter parameters.
5. Method according to claim 1. 1, 2, 3 or 4 characterized in that the modifiers or particles of the ceramic or chemical compounds in the form of grains, platelets and fibers are added to the plastics or their modifications during the mixing step in the proportions necessary to obtain the desired sintering parameters.
6. Method of claim 1, 2, 3, 4 or 5 characterized in that the input material particles of fixed parameters are placed directly in the ironing mold.

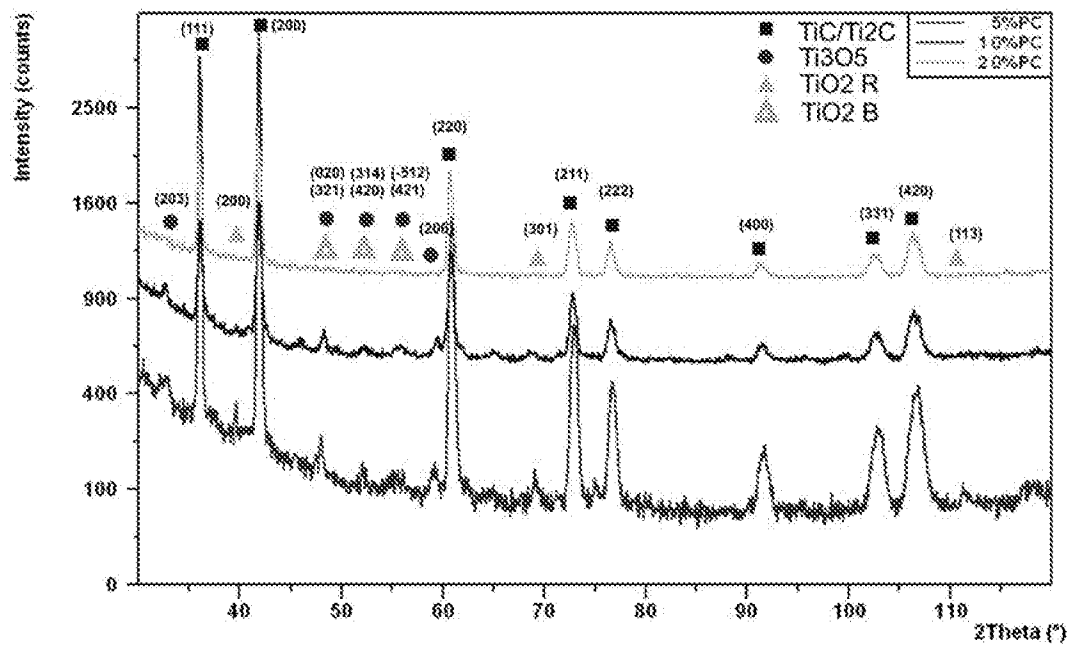


fig. 1

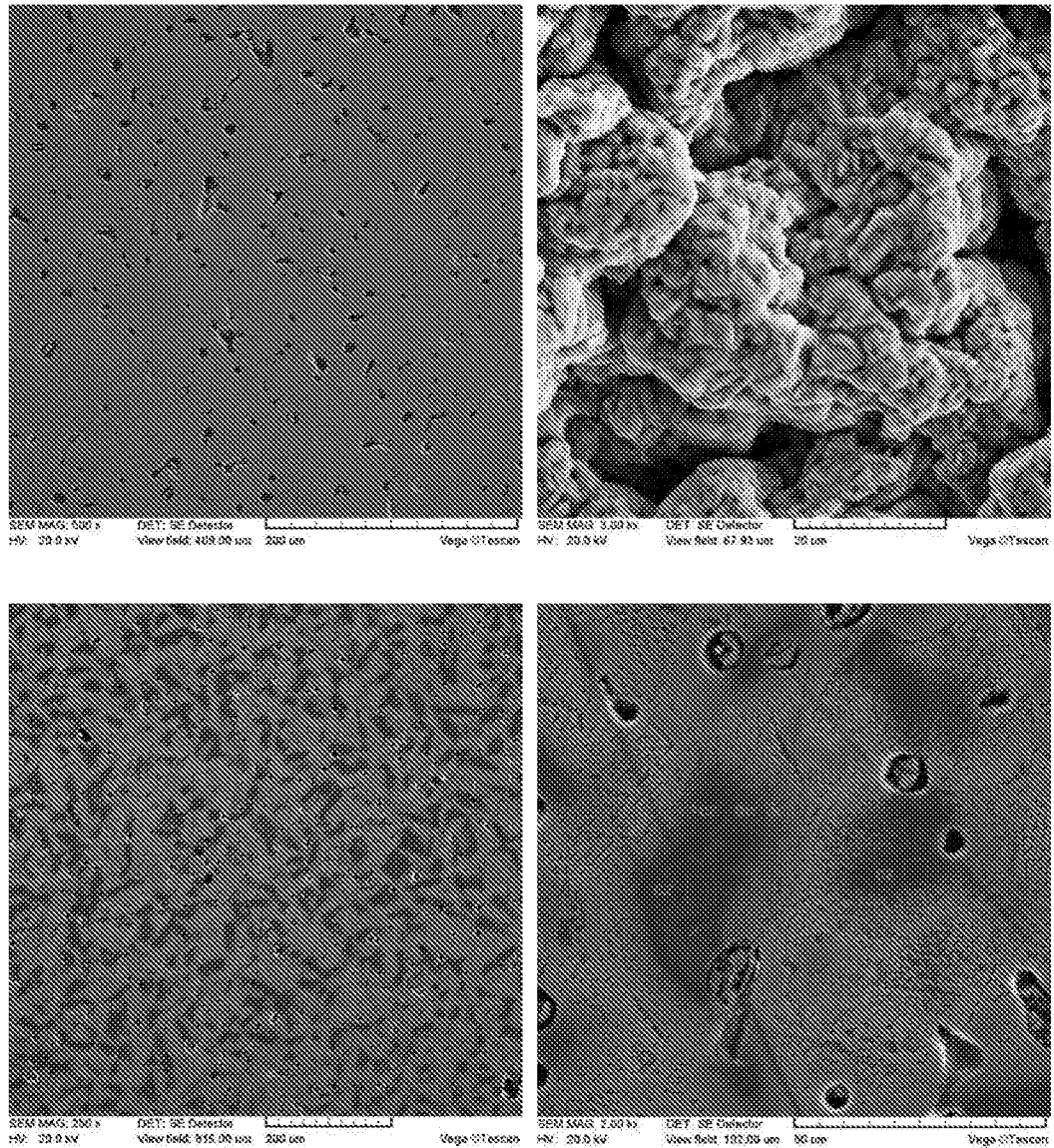


fig. 2

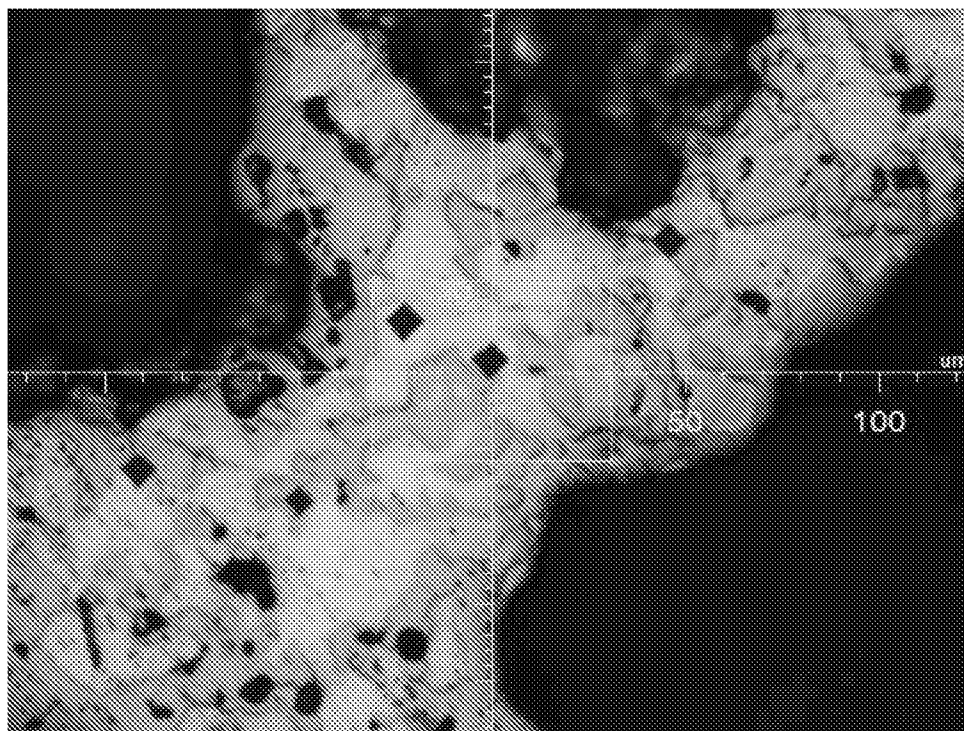


fig. 3

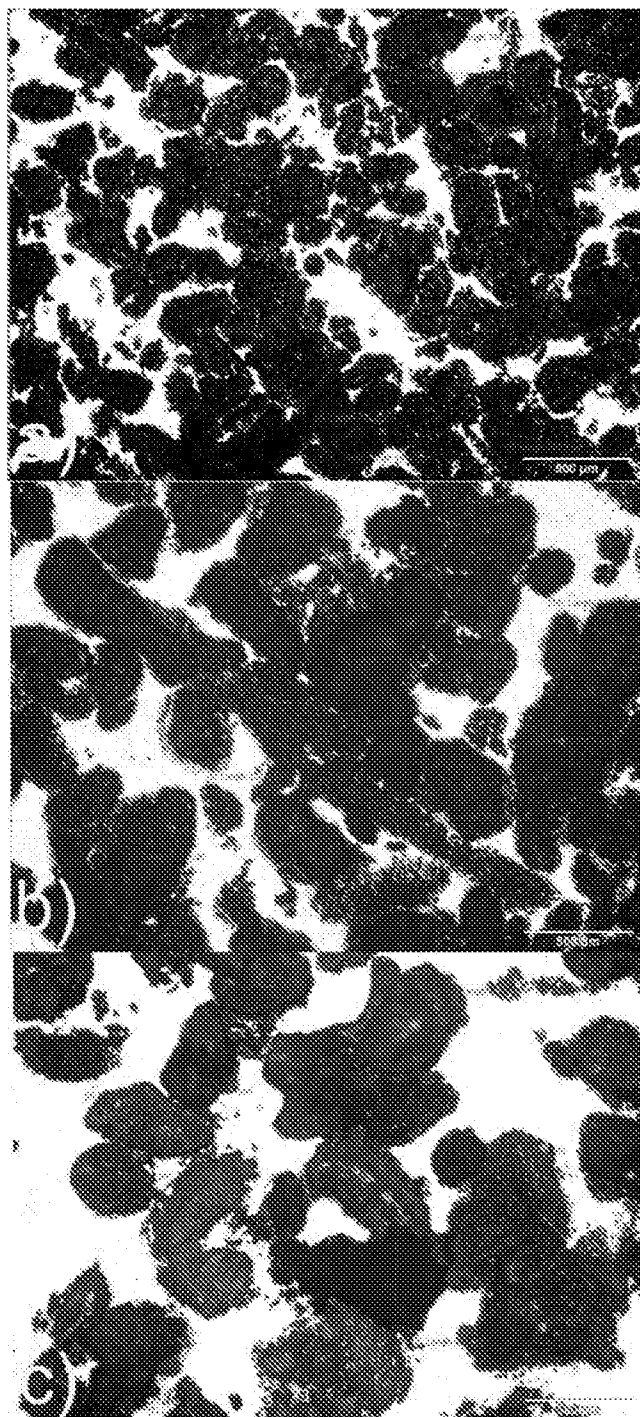


fig. 4

INTERNATIONAL SEARCH REPORT

International application No.

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A. CLASSIFICATION OF SUBJECT MATTER

B22F3/11 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B22F3

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Epodoc

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB714560 A (THOMPSON PROD INC) 1954-09-01 the whole document	1-6
Y	EP0639540 A1 (FIAT AUTO SPA [IT]) 1995-02-22 the whole document	1-6
Y	WO02066693 A1 (ISOTIS NV [NL]; LI JIA PING [NL]; LAYROLLE PIERRE JEAN FRANCOIS [NL]; DE GROOT KLAAS [NL]) 2002-08-29 the whole document	1-6



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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“E” earlier application or patent but published on or after the international filing date

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“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		IT1260928 (B)	1996-04-29
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