



US 20040146424A1

(19) **United States**(12) **Patent Application Publication**

Nelles et al.

(10) **Pub. No.: US 2004/0146424 A1**(43) **Pub. Date: Jul. 29, 2004**(54) **PRODUCTION OF COMPONENT PARTS BY METAL INJECTION MOULDING (MIM)**

(86) PCT No.: PCT/DK02/01460

(30) Foreign Application Priority Data

(76) Inventors: **Heinz Nelles**, Inden (DE); **Volker Bader**, Huckelhoven (DE); **Hans-Peter Buchkremer**, Heinsberg (DE); **Ariane marjam Ahmad-Khanlou**, Melissa (GR); **Martin Bram**, Julich (DE); **Detlev Stover**, Niederzier (DE)

Apr. 24, 2001 (DE)..... 10120172.9

Publication Classification(51) Int. Cl.⁷ B22F 3/10

(52) U.S. Cl. 419/37

(57) **ABSTRACT**

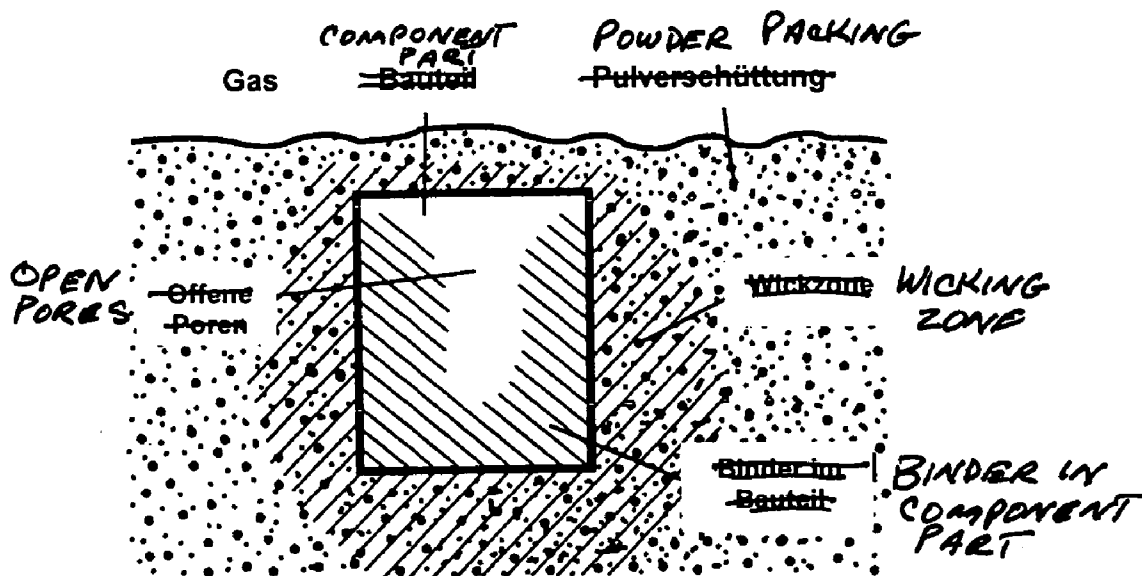
The invention relates to a method for producing component parts with a high degree of dimensional precision, made of NiTi-shape memory alloys. The invention makes it possible to apply a known metal injection moulding method to NiTi-shape memory alloys by adapting the binding system, temperature control and reducing the time necessary for debinding.

Correspondence Address:

THE FIRM OF KARL F ROSS**5676 RIVERDALE AVENUE****PO BOX 900****RIVERDALE (BRONX), NY 10471-0900 (US)**

(21) Appl. No.: 10/476,066

(22) PCT Filed: Apr. 20, 2002



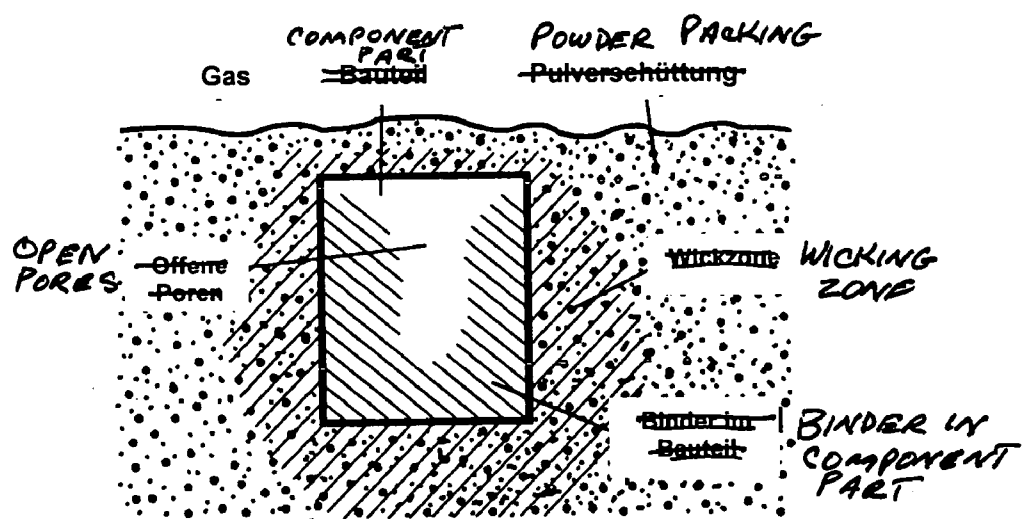


FIGURE 1

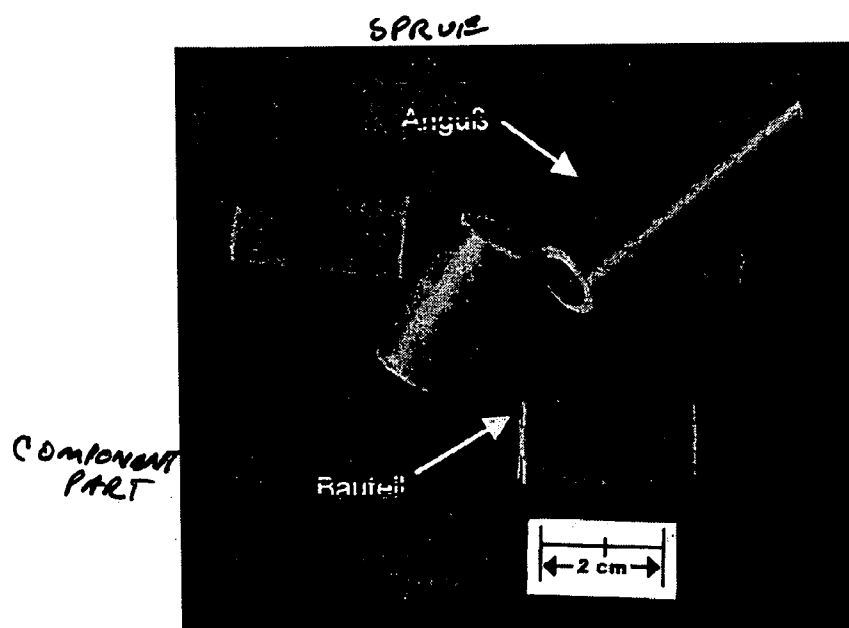


FIGURE 2

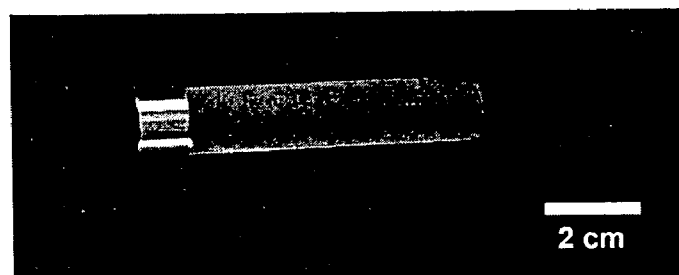


FIGURE 3

PRODUCTION OF COMPONENT PARTS BY METAL INJECTION MOULDING (MIM)

[0001] The invention relates to a method of producing component parts, especially a method for producing component parts to near final dimensions with the aid of metal injection molding.

STATE OF THE ART

[0002] Metal injection molding (MIM=Metal Powder Injection Molding), also called metal powder injection, is known for a method of mass producing metallic component parts, especially for the manufacture of such component parts to near final contours (NNS=near net shape) R. M. German, A Bose (editors): "Injection Molding of Metals and Ceramics", New Jersey, Metal Powder Industries Federation MPIF (1997)).

[0003] The MIM process allows small to middle size complex shaped parts to be produced in large numbers in an economical and automated manner. The MIM process supplies component parts with a density of 95 to 98% of the theoretical density and which with subsequent hot isostatic pressing can produce bodies (without encapsulating material) with a density of 100%.

[0004] The method encompasses the plastification of metal powder with a spherical or irregular morphology (powder particle sizes of 5 to 300 μm) by means of a binder system to a so-called feed stock. The homogenization of the feed stock is effected in a kneader. Thereafter the feed stock is fed to the injection molding machine. In a heated zone, a portion of the binder system (for example suitable waxes) is melted. A worm conveys the thermoplastic mass to a separable mold. After termination of the mold filling, the liquid phase solidifies again and enables the removal of the component part from the mold. The removal of the binder system is effected by a debinding step preceding the sintering. Depending upon the binder system, the additives are removed from the component parts in different ways.

[0005] Distinction can be made between thermal debinding methods (melting out or decomposing via the gas phase), solvent extraction as well as catalytic debinding. There follows the sintering process in which by diffusion processes, a compaction of the component part to up to 98% of the theoretical density can be reached. Because of the high binder content upon sintering significant shrinkage (15 to 20%) can arise. The control of the shrinkage ratio is one of the significant requirements in the production of near-net-shape component parts.

[0006] Typically suitable material for the metallic components in metal powder injection are stainless steels, carbon steels, tool steels or alloy steels, although ferrites, tungsten carbide and mixtures of copper/bronze, cobalt/chromium and also tungsten/copper are possible.

[0007] Shape memory alloys are metals which, after a deformation, again assume their original form when one heats them to a certain temperature. During this process, significant forces can arise. (W. J. Buehler, J. V. Gilfrich, R. C. Wiley: Ocean Engineering 1 (1968), 105). Perhaps the most well known are nickel-titanium alloys.

[0008] Possible fields of use for shape-memory alloys are micromanipulators and robotic actuators which can imitate

the flowing movements of the human musculature. In the steel-reinforced concrete structures, sensors of shape memory alloys can be used which can counteract the stresses arising in the interior because of cracks in the concrete or corrosion in the steel reinforcement bar.

[0009] Up to now, shape memory alloys based on the intermetallic phase NiTi were preferably fabricated by melt metallurgy. The shape was conventionally imparted by the mechanical machining of castings of NiTi material made by melt metallurgy and the method has been limited in that the alloys in the martensitic state have a high yield strength and thus a poor machinability. As a consequence the after-machining of melt metallurgy fabricated component parts has been possible only with a high expenditure of time and a high degree of tool wear.

[0010] The use of the metal injection molding process also for NiTi shape memory alloys has been a problem since apart from economical production rates, all of the small impurity contents required in the end product for the shape memory properties had to be insured. The difficulties of fabricating NiTi component parts by metal injection molding (MIM) is that the contents of oxygen and carbon must be held as low as possible. High impurity contents give rise to a reduced sintering activity of the metal powder and diminish the properties of the material in the sintered component part (for example by embrittlement).

[0011] A further important precondition for the production of NiTi shape memory alloy is the exact and reproducible setting of the alloy composition. Even minor deviations in the composition lead to significant variations in the characteristic properties (for example the transformation temperature).

OBJECT AND SOLUTION

[0012] The object of the invention is to provide an effective and low cost process for the near net shape fabrication of component parts from a prealloy NiTi shape memory alloy. Furthermore, it is the object of the invention to provide materials necessary for the process.

[0013] The objects are achieved with a method and the totality of the features of the main claim. Advantageous embodiments of the method and the materials required therefor are found in the dependent claims which respectively relate back to it.

SUBJECT OF THE INVENTION

[0014] The method according to the invention for the near net shape fabrication of component parts of prealloy NiTi shape memory alloys encompasses the following steps. Prealloy NiTi powder is mixed with a thermoplastic binder system to a feed stock. The feed stock is brought into the mold of the component part by an injection stage. The component part is exposed to a capillary-active substance, is predependent and then subjected to a thermal binding process. There follows a sintering to the finished component part.

[0015] An advantageous variant of the method is directed to the use of a two-component binder on a wax basis, especially a two-component binder of an amide wax and a polyolefin wax in a suitable composition. The amide wax influences the flow characteristics of the feed stock and

serves for the plastification thereof while the polyolefin serves for stabilization of the feed stock and contributes to the component part which is obtainable therefrom. Injection molding masses with viscosities of about 5 to 30 Pa.s can be injected. The very good flowability of the mass enables a rapid injection as well as a cavity-free and defect-free filling of even complex mold cavities with undercuts.

[0016] A further advantage is the high yield with respect to the material, since all injection byproducts which may arise can be recycled again to the fabrication process without loss of quality.

[0017] This increases the economy of the process, especially with respect to the processing of expensive materials.

[0018] The debinding process should be considered as a further process step. In this process step, the plastifying component (amide wax) is predebinded in a capillary [wick-ing] material at 120 to 150° C. This gives rise to a partial debinding of the entire green body. This process lasts about two hours. There then follows a thermal debinding of the components at about 480° C. for 10 hours. Depending upon the material used, the capillary-active substance can be sand or ceramic powder, (for example ZrO_2 , SiO_2 , SiC , Si_3N_4 or Al_2O_3). The separating agent between the capillary-active material and the component part can be filter paper which turns to ash without a residue during the debinding process.

[0019] The advantage of the manufacturing process according to the invention resides in that the percentages of carbon and oxygen can be held so low that the requirements for good shape memory properties are satisfied.

[0020] In experiments, carbon contents of, for example, 1400 ppm, and oxygen contents of 2300 ppm are obtained (Table 1). With these impurity levels, the reversible austenite-martensite transformation which is important for the shape memory properties can be detected by DSC (differential scanning calorimetry) measurements.

[0021] With the method of the invention, Ni-Ti component parts of a density of $\leq 95\%$ of solid density can be reproducibly made.

Special Descriptive Parts

[0022] Metal powder injection molding (MIM), also designated metal powder injection, is a powder metallurgical shape-imparting process which enables the low cost near net shape production of very complicated shapes in a rational and automatable manner. In addition, the powder injection is characterized by a high yield with respect to the starting material, thereby ensuring an efficiency utilization of the prealloyed NiTi powder which up to now has been extremely expensive since any sprue waste and scrap which can arise can be recycled to the process. The process combines the advantages of injection molding of thermoplastics (known from plastic fabrication) with the metal art possibilities of powder metallurgy.

[0023] 1. Powder and Feed Stock Production

[0024] For the production of a suitable powder, several factors are definitive. A primary condition is a high purity of the starting powder since an increase in impurities like oxygen, carbon and nitrogen in the powder during the process operations is unavoidable. This can result in the processing of titanium alloys, which have a high affinity to

these elements, to the formation of oxides, carbides and nitrides. These in turn influence the shape memory characteristics and give rise to an embrittlement of the material. In the normal case, powder of the particle size (ps) $\leq 25 \mu\text{m}$ is used. Coarser powder leads to lower final densities. The powder is processed with heatable kneaders with addition of the respective binder systems to the feed stock. The binder has the purpose of imparting to the powder the correct Theological characteristics in the injection stage and ensures the formation of a green body which is stable and can be handled. However, an important requirement for the characteristics of the component part is a residue-free removal of the binder. The selection of the binder is determinative of the quality of the product and thus the correct binder composition can be seen as "know how". Since the aforementioned requirements of the binder system cannot be achieved alone by a single system, as a rule a multicomponent system is used so as to ensure the requisite viscosity upon injection and in addition, a sufficient stability of the green body during the debinding or sintering. The component parts in the green state should be free from injection effects like internal gas passages and piping as well as mixture-separation inhomogeneities. In addition, the binder system must be of good plasticity and have elastic properties so that the samples do not develop solidification cracks as a result of different thermal expansion characteristics of the binder and the powder upon cooling. This can be achieved through control of the process as well as through control of the process as well as through the choice of a suitable binder system. During the procedure, no chemical reaction between the powder and binder should arise and a good wettability of the powder by the binder should develop. Generally the following binder systems which differ significantly as to the debinding process and are known to have been found to be suitable:

[0025] Thermoplastic binders;

[0026] Polymerization binders;

[0027] Gel-forming binders;

[0028] Extraction binders;

[0029] Duroplasts [Thermosetting binders].

[0030] The use of thermoplastic binders has been found to date to have the most widespread applications. To this belong such commercially available polymers as polyethylenes, polystyrenes, polypropylenes and waxes. Waxes or low molecular-weight polymers are best as main components.

[0031] The starting powder used in the method can for example be a commercially obtainable NiTi powder atomized from the melt with a particle size $\leq 25 \mu\text{m}$ and spherical particles as advantageous binder components, the thermoplastic amide wax (as plastifier) and polyolefin (as stabilizer) are significant. The advantage obtained is that it is possible to use a purely thermal debinding which simplifies the process, reduces the time for producing the product and thus can be cost saving. The expense of an intermediate step, like catalytic debinding or solvent extraction is thus avoided in this case.

[0032] 2. Debinding

[0033] The debinding process is an important process step for achieving the quality of the finished parts. The time

intensity of the process influences the cost factor of the overall process. The debinding process depends upon the binder system which is respectively used.

[0034] With the thermal debinding according to the invention, the binder system is liquefied by heating. The liquid binder is removed from the surface of the mold whereby the concentration gradient arises from the interior of the shaped part to the surface. With the aid of the capillary forces, the binder is continuously transported from the interior to the surface, giving rise to a continuous debinding.

[0035] As a very effective method for the removal of the wax, a capillary force induced sucking (wicking) of the wax in a temperature range between 120° C. and 150° C. has been found to be satisfactory. For this we operate with a powder packing whose particle distribution lies specifically below that of the starting material. The embedding of the shaped part reduces the debinding time significantly and effects a stabilization of the component body in addition.

[0036] Through the capillary forces, the melted wax is sucked out of the component body. The use of the filter paper supports this effect and protects the component parts against adhesion of the wicking material used. The binder system is so constructed that after the predebinding process, the residual plastifying component is driven out or evaporated. A minor residual binder proportion between the individual particles ensures the shape stability of the green body until this residual binder is driven off by the combined debinding/sintering step. The component part, after the wicking process, can be handled and can be removed from the sand bed for the sintering and can be placed upon ZrO₂ sintering supports for the sintering process.

[0037] 3. Sintering

[0038] In the starting phase of the sintering, the residual binder which remains in the green body must be heated sufficiently to drive it out. For this purpose, the shaped part is removed from the wicking sand, placed upon a sintering support and slowly heated up to the debinding temperature and held at this temperature for 1 to 2 hours. Subsequently there follows a sintering in the same process step. The sintering is effected under a protective gas or in vacuum. The sintering density which is reached is reproducible in the region of about 95% of theoretical density. The theoretical density can be reached by an additional HIP (hot isostatic pressing) process.

EXAMPLES

Example 1

[0039]

1400 g	NiTi - powder
64.4 g	Amide wax
42.9 g	Polyolefin

[0040] Total binder proportion: 7.12% by weight=34 volume %.

Example 2

[0041]

1800 g	NiTi - powder
64.4 g	Amide wax
42.9 g	Polyolefin

[0042] Total binder proportion: 5.63% by weight=28 volume %.

[0043] Wicking Parameter:

[0044] in ZrO₂ sand with a particle size <10 μm with use of filter paper.

[0045] a flowing argon atmosphere or vacuum.

[0046] up to 4 hours at 120°- 150° C.

[0047] Then the samples are removed from the wicking sand.

[0048] Debinding/sintering parameters (sintering support ZrO₂):

[0049] at a rate of 1 K/minute from room temperature to 450° C. under a flowing argon atmosphere,

[0050] holding time at 450° C.: 2 hours,

[0051] heating at a rate of 5 K/minute to 1250° C.,

[0052] holding time 5 hours,

[0053] all under a protective gas (argon, 1270 mbar).

[0054] The sinter density achieved corresponded to 95% of theoretical density.

TABLE 1

Impurities of carbon, nitrogen and oxygen in the starting material as well as after debinding or sintering of the component parts.			
	C % by weight	N % by weight	O % by weight
NiTi - Starting State	0.0677	0.0018	0.0763
After Debinding	0.0953	0.0028	0.2431
After Sintering	0.1460	0.0051	0.2308

FIGURES

[0055] FIG. 1: Diagram of the wicking process.

[0056] FIG. 2: Shape bodies after the injection stage.

[0057] FIG. 3: Component parts following final sintering other geometries than in FIG. 2).

1. A method of making component parts from prealloyed NiTi shape memory alloys with the use of metal injection molding with the steps of

prealloyed NiTi powder is mixed with a thermoplastic binder to a feed stock, using an injection stage, the thus formed feed stock is introduced into the mold for the component parts,

the component parts are brought into contact with a capillary-active material and are predebinded,

the component parts are then subjected to a thermal debinding process,

the component parts freed from binder are sintered.

2. A method according to the preceding claim, characterized by the use of a two-component binder on a wax basis.

3. A method according to one of the preceding claims, characterized by a binder encompassing polyolefin.

4. A method according to one of the preceding claims, characterized by a binder encompassing 50 to 65% of amide wax and 35 to 50 weight % polyolefin.

5. A method according to one of the preceding claims, characterized by a binder with a content of 64.4 weight % amide wax of 42.9 weight % polyolefin.

6. A method according to one of the preceding claims, characterized by a feed stock with a viscosity between 5 and 30 Pa.s.

7. A method according to one of the preceding claims, characterized by a partial debinding process in which initially an amide wax is removed from the interior of the green body.

8. A method according to a preceding claim in which the amide wax is removed by capillary force induced sucking up with the aid of a powder packing.

9. A method according to a preceding claim in which the powder packing has a particle size which is less than the particle size of the NiTi powder used.

10. A method according to one of the preceding claims 7 to 9 in which a filter paper is interposed between the green part and the powder packing.

11. A method according to one of the preceding claims 7 to 10 using a ZrO₂ powder packing.

12. A method according to one of the preceding claims 7 to 11 in which the powder packing has a particle size which is less than the particle size of the metal powder used, especially with particle sizes in the range of 0.01 to 1 μ m.

13. A method according to one of the preceding claims 7 to 12 in which the debinding process is carried out at temperatures between 120° C. and 480° C.

* * * * *