The present invention relates to a metal injection molding process.

Metal injection molding (MIM, also known by the generic term powder injection molding, PIM) is a powder metallurgical process in which a molding is produced by injection molding of a thermoplastic injection molding material which contains metal powder and usually at least 30% by volume of a thermoplastic binder, the binder is then removed from said molding and the molding is then sintered to give the finished workpiece. Metal injection molding combines the advantages of shaping by injection molding, known from plastics technology, with those of classical powder metallurgy. In classical powder metallurgy (often referred to as P/M), metal powder, to which up to 10% by volume of lubricant, such as oil or wax, has often been added, is brought to the desired shape by compression molding and the molding is then sintered. The advantage of the powder metallurgical processes is the freedom of choice of material. In powder metallurgical processes, on sintering a metal powder mixture, it is possible to produce materials which cannot be prepared by fusion metallurgical processes. A substantial disadvantage of classical powder metallurgy by compression molding and sintering is that it is not suitable for the production of workpieces having relatively complex geometrical shapes. For example, shapes with undercuts, i.e. indentations transverse to the compression direction, can not be produced by compression molding and sintering. In injection molding, by contrast, virtually any desired shape can be produced. On the other hand, a disadvantage of metal injection molding is that anisotropies occasionally occur in the mold in the case of relatively large workpieces, and that a separate step has to be carried out for removing the binder. Metal injection molding is therefore predominantly used for relatively small workpieces having a complicated shape.

An important parameter for powder metallurgical techniques is the particle size of the metal powder used or the components of the metal powder mixture used. In general, a d90 value in micrometer units is stated in this context. It means that 90% by weight of the relevant powder are present in the form of particles having a particle size of not more than this d90 value. Occasionally, analogous d10 or d50 values are stated. (From time to time, the capital letter D is also used, which therefore denotes the value as D10, D50 or D90.) In the case of spherical particles, the measured particle size corresponds to the sphere diameter; in the case of nonspherical particles, the method of measurement (usually laser light diffraction) necessarily measures an effective diameter of the particles which corresponds to the diameter of spherical particles of the same volume.

In the metal injection molding of iron-containing materials, comparatively fine metal particles, in particular iron or steel particles, are always used. Although the fine metal particles are comparatively expensive and are difficult to handle owing to their tendency to agglomerate and their pyrophoric properties, they have better sintering properties. This is important particularly in the case of low-alloy steels (in the context of this invention, low-alloy steels are understood as meaning steels having an iron content of at least 90% by weight, i.e. a content of alloy elements

of not more than 10% by weight) since high-alloy steels can typically be considerably better sintered, i.e. give homogeneous and dense sintered workpieces more easily than low-alloy steels. In the case of metal injection molding, particularly in the production of sintered shaped articles from low-alloy steels, iron or steel powders having a d90 value of from 0.5 to 20 micrometers are therefore always used, and only very seldom those having a d90 value of up to not more than about 30 micrometers. Owing to the comparatively high binder content of the ready-to-use metal injection molding material, which prevents contact of the individual metal particles with atmospheric oxygen, the pyrophoric properties of fine metal particles in powder injection molding materials can be controlled. In classical powder metallurgy, on the other hand, the fine powders with their tendency to agglomerate usually lead to nonuniform filling of the mold, and pyrophoric properties of the metal powder are not tolerable. In classical powder metallurgy by compression molding and sintering, comparatively coarse particles having a d90 value above 40 micrometers are therefore always used.

A. R. Erickson and R. E. Wiech: Injection Molding, in: ASM Handbook, Vol 7, Powder Metallurgy, American Society for Metals, 1993 (ISBN 0-87170-013-1) give an overview of the metal injection molding technique. R. M. German and A. Bose: Injection Molding of Metals and Ceramics, Metal Powder Industries Federation, Princeton, New Jersey, 1997 (ISBN 1-878-954-61-X) summarize the powder injection molding technique (metal and ceramic), in particular Chapter 3 gives an overview of the powders used for powder injection molding. L. F. Pease III and V. C. Potter: Mechanical Properties of P/M Materials disclose typical alloys for powder metallurgical processes and the achievable properties of the workpieces thus produced.

EP 446 708 A2 (equivalent: US 5,198,489), EP 465 940 A2 (equivalent: US 5,362,791), EP 710 516 A2 (equivalent: US 5,802,437) and WO 94/25 205 (equivalent: US 5,611,978) disclose various injection molding materials for use in metal injection molding processes, and metal injection molding processes in which the binder is removed catalytically from injection molded parts, which are then sintered. EP 582 209 A1 (equivalent: US 5,424,445) describes certain dispersants for use as assistants in powder injection molding materials.
WO 01/81 467 A1 discloses a binder system for metal injection molding. WO 96/08 328 A1, on the other hand, discloses a typical composition for classical powder metallurgy by compression molding and sintering, with up to 10% by weight of a polyether wax as a lubricant.

There is still a need for more a widely applicable and especially economical injection molding materials and injection molding processes. It is an object of the present invention to provide an economical and widely applicable metal injection molding process and an injection molding material for this purpose.

We have found that this object is achieved by a metal injection molding material which contains

a) from 40 to 70% by volume of metal powder, including at least 50% by weight, based on the total amount of metal, of an iron-containing powder, at least 90% by weight, based on the amount of this iron-containing powder, of the particles of which have an effective diameter of at least 40 micrometers,

b) from 30 to 60% by volume of a thermoplastic binder and

c) from 0 to 5% by volume of a dispersant and/or other assistants.

We have furthermore found a metal injection molding process wherein this injection molding material is shaped by injection molding, the injection molded parts are freed from the binder and said parts freed from the binder are sintered.

The novel metal injection molding material contains a comparatively extremely coarse iron or iron alloy powder. The present invention is based on the knowledge that, in spite of a contrary opinion on the part of those skilled in the art, such a coarse metal powder also leads to satisfactory results in metal injection molding, and does so also and in particular in the production of sintered shaped articles from low-alloy steels. The coarse metal powders lead to a very considerable cost reduction for the metal injection molding materials, and their handling is substantially easier. The sintered shaped articles produced by the novel process have properties which are at least as good as sintered shaped articles produced by classical powder metallurgy, but can also be produced with very complex geometries.

The novel metal injection molding material generally contains at least 40, preferably at least 45, % by volume and in general not more than 70, preferably not more than 60, % by volume, based in each case on the total volume of the injection molding material, of metal powder. As is generally customary in powder metallurgy, said metal powder may be a single pure metal powder, a mixture of different pure metal powders, a pure powder of a metal alloy, a mixture of different metal alloy powders or a mixture of one or more pure metal powders with one or more metal alloy powders. The overall composition of the powder determines the overall composition of the finished sintered shaped article and is chosen according to the desired composition, it being possible, as is also customary in powder metallurgy, also to establish the desired carbon, oxygen and/or nitrogen content of the finished sintered shaped article during the sintering.

At least one of the metal powders contained in the novel injection molding material contains iron. The iron-containing powder is preferably a low-alloy steel or pure iron. In one embodiment, the metal powder in the novel powder injection molding material consists completely of iron, alternatively with a carbon content of from 0 to 0.9% by weight. In another embodiment, the metal powder consists of a low-alloy steel which contains from 0 to 0.9% by weight of carbon, from 0 to 10% by weight of nickel, from 0 to 6% by weight of molybdenum, from 0 to 11% by

weight of copper, from 0 to 5% by weight of chromium, from 0 to 1% by weight of manganese, from 0 to 1% by weight of silicon, from 0 to 1% by weight of vanadium and from 0 to 1% by weight of cobalt, the remainder being iron, and the total amount of the elements present, excluding iron, being not more than 10% by weight. In this case, the total amount of the metal powder contained in the novel metal injection molding material preferably comprises at least 90% by weight of iron.

At least 50% by weight, based on the total amount of metal powder, of the metal powder in the novel injection molding material comprise the iron-containing powder. Preferably, at least 60, particularly preferably at least 80, % by weight, based on the total amount of metal powder, of the metal powder in the novel powder injection molding material comprise the iron-containing powder. In one embodiment of the novel powder injection molding material, exclusively the iron-containing powder is used as metal powder.

In addition to the iron-containing powder, it is however also possible to use other metal powders which either also contain further iron in addition to other elements or even consist of iron. For example, a low-alloy steel is produced by the master alloy technique from iron powder and a powder comprising an iron-free alloy of the desired alloy elements or from a corresponding high-alloy steel or corresponding mixtures (prealloyed or partially alloyed powder). These techniques are known. All that is decisive for the present invention is that at least 50% by weight of the metal powder present in the powder injection molding material comprise an iron-containing powder, once again at least 90% by weight, based on the amount of this iron-containing powder, of the particles of which have an effective diameter of at least 40 micrometers. In other words, the metal powder in the novel metal injection molding material contains at least 50% by weight of an iron-containing powder having a particle size, expressed as the d90 value, of at least 40 micrometers. The proportion of the metal powder which is not formed by this iron-containing powder is any desired metal powder or metal powder mixture suitable for metal injection molding, and is chosen according to the desired final composition of the sintered shaped articles to be produced.

The iron-containing powder in the novel injection molding material consists of particles of which at least 90% by weight, based on the amount of this iron-containing powder, have an effective diameter of at least 40 micrometers. Preferably, this effective diameter is at least 50, particularly preferably at least 60, micrometers. In other words, the iron-containing powder has a d90 value of at least 40, preferably at least 50, particularly preferably at least 60. A suitable d90 value is, for example, 70. The d90 value is determined by means of laser light diffraction according to ISO/DIS standard 13320 Particle Size Analysis Guide to Laser Diffraction.

The metal powders used in the novel injection molding material are customary commercial products.

The novel metal injection molding material generally contains at least 30, preferably at least 40, % by volume and in general not more than 60, preferably not more than 55, % by volume, based in each case on the total volume of the injection molding material, of a thermoplastic binder. The substantial object of the binder is to impart thermoplastic properties to the powder injection molding material, and an important criterion for the suitability of a certain thermoplastic as the binder is the possibility of removing it after the injection molding. Various binders and methods for removing binders from powder injection moldings are known, for example thermal removal of binder by pyrolysis of the thermoplastic, removal of binder by the use of a solvent or catalytic removal of binder by catalytic decomposition of the thermoplastic. Any thermoplastic binder known for powder injection molding can be chosen as a thermoplastic binder for the novel powder injection molding material.

Conveniently, a catalytically removable binder is used. Such binder systems are usually based on polyoxymethylene as the thermoplastic. Polyoxymethylene depolymerizes under acid catalysis and can thus be removed from the injection molded parts rapidly and at comparatively low temperatures. The thermoplastic binder preferably consists of a mixture of from 50 to 100% by weight of a polyoxymethylene homo- or copolymer and from 0 to 50% by weight of a polymer which is immiscible with the polyoxymethylene homo- or copolymer and can be removed thermally without a residue, or of a mixture of such polymers. Such binders are known and are disclosed, for example, in EP 446 708 A2, EP 465 940 A2 and WO 01/81467 A1, which are hereby incorporated by reference.

The novel powder injection molding material may also contain dispersants and/or other assistants in an amount of up to 5% by volume. Preferably, it contains at least 1% by weight of dispersants and/or other assistants. Dispersants serve for preventing separation processes and are disclosed, for example, in the publications referred to above and in EP 582 209 A1, which is likewise hereby incorporated by reference. Other assistants are usually added for influencing rheological properties of the powder injection molding material. Occasionally, carbon, generally in the form of graphite or in the form of pyrolyzable polymers, is also added in order to establish the carbon content of the sintered shaped article during sintering. These measures are known, for example from the publications referred to above.

The novel powder injection molding material is usually prepared by mixing its components. The preparation is preferably effected by thorough mixing in the melt or at least in pasty form. All apparatuses in which pasty to liquid substances can be thoroughly mixed are suitable for this

purpose, for example heatable kneaders. The novel powder injection molding material is produced in the form of particles which are suitable for feeding conventional injection molding machines, for example strands, extrudates, pellets or crushed kneaded material.

The novel powder injection molding process is carried out in the same way as conventional powder injection molding processes. For this purpose, the novel injection molding material (i.e. the feedstock) is shaped by injection molding to give green compacts, the injection molded parts are freed from the binder (i.e. binder removal) and the brown compacts thus produced from the green compacts, and the brown compacts are sintered to give finished sintered shaped articles.

The molding of the feedstock is effected in a conventional manner using customary injection molding machines. The moldings are freed from the thermoplastic binder in a conventional manner, for example by pyrolysis or by a solvent treatment. The binder is preferably removed catalytically from the preferred novel injection molding material comprising a binder based on polyoxymethylene, by subjecting the green compacts in a known manner to a heat treatment with an atmosphere containing a gaseous acid. This atmosphere is prepared by vaporizing an acid with sufficient vapor pressure, or more conveniently by passing a carrier gas, in particular nitrogen, through a storage vessel containing an acid, advantageously nitric acid, and then passing the acid-containing gas into the binder removal oven. The optimum acid concentration in the binder removal oven is dependent on the desired steel composition and on the dimensions of the workpiece and is determined in the individual case by routine experiments. In general, a treatment in such an atmosphere at from 20 to 180°C over a period of 10 minutes to 24 hours is sufficient for binder removal. Any residues of the thermoplastic binder and/or of the assistants which are still present after the binder removal are pyrolyzed during heating up to sintering temperature and are thus completely removed.

After the shaping and subsequent removal of the binder, the molding is sintered in a sinter furnace to give the sintered shaped article. The sintering is effected by known methods. Depending on the desired result, for example, sintering is effected under air, hydrogen, nitrogen or a gas mixture or under reduced pressure.

The composition of the furnace atmosphere which is optimal and for sintering, the pressure and the optimum temperature range depend on the exact chemical composition of the steel used or to be prepared and are known or, in the individual case, can be readily determined on the basis of a few routine experiments.

The optimum heating rates are readily determined by a few routine experiments and are usually at least 1, preferably at least 2, particularly preferably at least 3, °C per minute. For economic reasons, a very high heating rate is generally desirable. In order to avoid an adverse effect on

the quality of the sintering, however, a heating rate below 20°C per minute should generally be established. In certain circumstances, it may be advantageous to maintain, during the heating to the sintering temperature, a waiting time at a temperature which is below the sintering temperature, for example to maintain a temperature of from 500 to 700°C, for example 600°C, over a period of from 30 minutes to two hours, for example one hour.

The duration of sintering, i.e. the hold time at sintering temperature, is generally established so that the sintered shaped articles are sufficiently densely sintered. At conventional sintering temperatures and sizes of shaped articles, the duration of sintering is in general at least 15, preferably at least 30, minutes. The total duration of the sintering process substantially determines the production rate, and sintering is therefore preferably carried out so that, from the economic point of view, the sintering process does not take an unsatisfactorily long time. In general, the sintering process (including heating phase but without cooling phase) can be completed after at most 14 hours.

The sintering process is ended by cooling the sintered shaped articles. Depending on the composition of the steel, a certain cooling process may be required, for example very rapid cooling, in order to obtain high-temperature phases or to prevent separation of the components of the steel. For economic reasons, it is also generally desirable to cool very rapidly in order to achieve high production rates. The upper limit of the cooling rate is reached if an economically unsatisfactorily large amount of sintered shaped articles having defects caused by excessively rapid cooling, such as cracking, breaking or deformation, occur. Accordingly, the optimum cooling rate is easily determined in a few routine experiments.

After the sintering, any desired aftertreatment, for example sinter hardening, austenitization, annealing, hardening, heat treatment, carburization, case hardening, carbonitriding, nitriding, steam treatment, solution heat treatment, quenching in water or oil and/or hot isostatic pressing of the sintered shaped articles or combinations of these treatment steps, can be carried out. Some of these treatment steps, for example sinter hardening, nitriding or carbonitriding, can also be carried out in a known manner during the sintering.

Examples

Example 1: Production of a molding from Fe-Ni-C steel comprising 2% by weight of nickel and 0.5% by weight of C:

In a heatable laboratory kneader, 4 400 g of iron powder (type ASC 300 from Höganäs AB, 26383 Höganäs, Sweden, with d50 = 30 micrometers, d90 = 70 micrometers, 0.01% by weight of carbon), 90 g of nickel powder (d90 = 26 micrometers) and 2.2 g of graphite powder (d90 = 8 micrometers) and a binder comprising 500 g of polyoxymethylene, 70 g of polypropylene and 30 g of a dispersant were mixed by kneading and, on cooling, crushed to give granules. The granules were processed using a screw-type injection molding machine to give tensile test bars having a length of 85.5 mm and a diameter of 4 mm (according to MPIF standard 50, 1992). The injection moldings were subjected to catalytic binder removal in a chamber oven at 110°C in a nitrogen atmosphere, to which 25 ml/h of concentrated nitric acid were metered. The samples were then sintered in dry nitrogen in an electrically heated furnace by heating at a heating rate of 5 K/min to 1360°C, holding at this temperature for one hour and slowly cooling in a furnace. The density of the samples was more than 7.1 g/cm^3. The metallographic investigation of transverse ground sections showed a ferritic/perlitic structure with elongated pores. The carbon content of the samples was 0.5% by weight.

The samples were heat-treated by austenitization at 870°C, oil quenching and annealing at 200°C for one hour. Their hardness thereafter was 43 HRC.

Example 2

Example 1 was repeated, except that 30% by weight of the coarse iron powder was replaced by carbonyl iron powder (d90= 10 micrometers). The density achieved after sintering was 7.3 g/cm^3 and the carbon content was 0.5% by weight. The structure was somewhat more uniform than in the case of the sample of example 1 and the proportion of elongated pores was smaller. After the heat treatment, a hardness of 46 HRC was reached.

Comparative example

Example 1 was repeated, except that the coarse iron powder was completely replaced by carbonyl iron powder (d90 = 10 micrometers). The density achieved after sintering was 7.6 g/cm^3 and the carbon content was 0.5% by weight. All pores were round and smaller than in examples 1 and 2. After the heat treatment, a hardness of 55 HRC was reached.

The examples show that, even with comparatively extremely coarse metal powders, properties of sintered shaped articles are achieved which are not at all inferior to the typical properties of shaped articles produced by compression molding and sintering and scarcely inferior to typical properties of conventional powder injection molded parts.

Metal powder injection molding material and metal powder injection molding method

We claim:-

1. A metal injection molding material which contains
   a) from 40 to 70% by volume of metal powder, including at least 50% by weight, based on the total amount of metal, of an iron-containing powder, at least 90% by weight, based on the amount of this iron-containing powder, of the particles of which have an effective diameter of at least 40 micrometers,
   b) from 30 to 60% by volume of a thermoplastic binder and
   c) from 0 to 5% by volume of a dispersant and/or other assistants.

2. A metal injection molding material as claimed in claim 1, wherein at least 90% by weight, based on the amount of the iron-containing powder, of the particles of the iron-containing powder have an effective diameter of at least 50 micrometers.

3. A metal injection molding material as claimed in claim 2, wherein at least 90% by weight, based on the amount of the iron-containing powder, of the particles of this iron-containing powder have an effective diameter of at least 60 micrometers.

4. A metal injection molding material as claimed in claim 1, wherein the total amount of the metal powder contained comprises at least 90% by weight of iron.

5. A metal injection molding material as claimed in claim 1, wherein the thermoplastic binder consists of a mixture of from 50 to 100% by weight of a polyoxymethylene homo- or copolymer and from 0 to 50% by weight of a polymer which is immiscible with the polyoxymethylene homo- or copolymer and can be removed thermally without a residue, or of a mixture of such polymers.

6. A metal injection molding process, wherein a metal injection molding material which contains
   a) from 40 to 70% by volume of metal powder, including at least 50% by weight, based on the total amount of metal, of an iron-containing powder, at least 90% by weight, based on the amount of this iron-containing powder, of the particles of which have an effective diameter of at least 40 micrometers,
   b) from 30 to 60% by volume of a thermoplastic binder and
   c) from 0 to 5% by volume of a dispersant and/or other assistants,

   is shaped by injection molding, the injection molded parts are freed from the binder and said parts freed from the binder are sintered.