

Method for Producing Molded Articles of Aluminum Alloys

The metal injection molding technology experienced a boom in recent years and has become an established technology for producing complex small parts, generating a worldwide annual turnover of approximately EUR 1 billion. The combination of the molding technology applied for plastic injection molding with various materials used in powder technology has opened up interesting new markets for many materials.

The production method essentially comprises the process steps described below. At first, a feedstock in the form of an injectable granulate, which consists of metal powder and a plastic component comprising at least two intimately mixed polymer components, is produced. This feedstock is then molded by plastic injection molding machines to obtain molded articles. These so called "green bodies" usually contain approx. 40 % by volume of a plastic binder, which is largely removed in the subsequent so called debinding (or "debinding") step. A residual binder component, the so called "backbone", remains and guarantees the residual strength of the article after debinding. The debinding can be achieved in various ways, for example thermally, using solvents, catalytically, etc., the selected process being carefully adapted to the plastic binder used in the granulate. After debinding, the article, the so called "brown body", is subjected to a sintering process, in the first step of which the residual "backbone" binder is usually thermally removed, whereafter the article is sintered and shrinks to form a nearly compact metal component. This technology is currently applied to high- and low-alloy steels, precious metals, hard metals, but also to ceramics.

Metal injection molding for aluminum materials has not yet been successfully established in industry, although there are patents relating to this technology; this is due to the fact that the sinter mechanisms of aluminum alloys are completely different from those of the above mentioned materials. Non-reducible oxides on the surface of aluminum powders constitute significant obstacles to sintering. For this reason, publications only describe an oxygen-free atmosphere.



A particular difficulty in connection with the above described processing of aluminum relates to the relatively low melting point of aluminum (660 °C), which is further lowered when alloying elements such as tin are added thereto. This results in the problem that debinding of the plastic component has to be completed at very low temperatures, making the suitable process time frame often too short for guaranteeing the plastic component's complete removal. If the plastic component is not completely removed, undesired reactions of organic residual components with metal components may take place, which interfere with the sintering process and thus impair the mechanical characteristics obtainable by the method.

Liu et al. in Powder Metallurgy 51, 78-83 (2008) describe a method in which tin, as an alloying metal, and magnesium blocks are added, the magnesium serving as "sacrificial metal", i.e. as an oxygen and humidity trap.

Against this background, the aim of the present invention consisted in developing a metal injection molding process for producing molded articles of aluminum materials with good mechanical characteristics in a simple and reproducible way.

DISCLOSURE OF THE INVENTION

The inventors have achieved this aim by providing a method for producing molded articles based on aluminum alloys by metal injection molding, said method comprising the following steps:

a) producing a feedstock by mixing the metals contained in the desired alloy in the form of metal powders and/or one or more metal alloy powders with a binder;

b) producing a green body by injection molding the feedstock;

c) producing a brown body by at least partially removing the binder from the green body by catalytic and/or solvent and/or thermal debinding;

d) sintering the at least partially debindered brown body to obtain the desired molded article;

the method of the invention being characterized in that the binder is completely removed in step c), wherein thermal debinding is carried out to remove the (residual) binder, optionally after having carried out one or more previous debinding steps, said

thermal debinding being carried out in an atmosphere containing at least 0.5 % by volume of oxygen, whereafter the thus obtained, completely debound (or debinded or debindered) brown body is sintered.

- 5 This method yields highly pure molded articles of aluminum alloys, as, due to the complete removal of the binder in step c), there are no undesired reactions of the plastic material with the alloying metals. The complete removal of the binder is achieved due to the presence of oxygen in the atmosphere, even at relatively low temperatures. Contrary to current teachings, according to which the presence of
- 10 oxygen is to be absolutely prevented, the inventors have found that a small portion of oxygen, of at least 0.5 % by volume, does not significantly increase the oxidation of the aluminum, but contributes to a faster and complete debinding. Depending on the composition of the powder mixture and the temperature conditions, an oxygen content, for example, between 20 and 100 % by volume is applied, which means that
- 15 it is even possible to use pure O₂ gas.

In addition to aluminum, the aluminum alloy contains one or more other metals which are not subject to any specific limitations. The alloy partners are preferably selected from the group consisting of magnesium, copper, silicon, and manganese, and are

20 particularly preferably contained at proportions of 0.5 to 25 % by weight, in order to obtain molded articles having the desired characteristics. Metals such as bismuth, tin, lead, indium, or zinc, or alloys such as Wood's metal, which have significantly lower melting points and which, in some cases, may serve as sintering aids lowering the temperature at which melting starts, are not required according to the present invent-

25 ion, but may still be added as alloying partners, if desired, in order to obtain sintered bodies of the respective alloys. It is particularly advantageous to use the other metals in the form of alloys with aluminum, i.e. as so-called master alloy powders.

According to the present invention, it is preferred to use binders which are known to

30 be removable at low temperatures, polyacetal-based binders, e.g. poly(oxymethylene) (POM) binders, are particularly preferred, for example as disclosed by BASF in EP 413,231, WO 94/25205, and particularly in EP 446,708, and commercially available

under the trademark Catamold®. It is desirable for the binder to have a high polyacetal percentage, consisting preferably of 50 to 95 %, even more preferably of 80 to 90 %, of polyacetal to promote the fast and complete removability at low temperatures and in the presence of oxygen. Alternatively, binder systems based on wax and polymers may be used, the wax as the main component being removed by a preceding solvent debinding, i.e. before carrying out the thermal debinding in the presence of oxygen according to the invention.

The debinding in step c) of the method of the invention may comprise a single thermal debinding step in the presence of oxygen in which the binder is completely removed. Alternatively, one or more preceding debinding steps may be carried out to remove the main proportion of the binder, followed by the thermal debinding step of the invention to remove the residual binder in the presence of oxygen. A preceding debinding step may also be a thermal debinding step – in the absence or also in the presence of oxygen. This means that it is also possible to carry out a multi-step thermal debinding process using different process parameters for debinding – for example at different temperatures or in different atmospheres, for example without and with oxygen or with air or with pure oxygen, etc.

In preferred embodiments of the invention, catalytic debinding and/or solvent debinding is carried out before the thermal debinding to remove the residual binder in the presence of oxygen in step c). In these preceding debinding steps, the main part of the binder is already removed from the composition so that only the "backbone" component remains to be removed by the subsequent thermal debinding.

Catalytic debinding is preferably carried out in the presence of at least one acid selected from nitric acid, oxalic acid, formic acid, and acetic acid, as these acids accelerate the complete removal of the preferred polyacetal binders by acidolysis without leading to undesired side reactions with the alloy components. In the case of solvent debinding, the main part of the binder is removed by extraction with a suitable solvent or mixed solvent, e.g. acetone, n-heptane, water, etc. According to the pres-

ent invention, it is particularly preferred to apply catalytic debinding using sublimated oxalic acid.

As already mentioned above, the thermal debinding process for removing the residual binder in step c) is carried out at a relatively low temperature in order to avoid oxidation reactions, particularly of the aluminum contained in the powder mixture. A relatively low temperature herein refers to a temperature which is significantly lower than the melting point of aluminum, preferably below 500 °C, more preferably between 100 and 420 °C. It is particularly preferred to set a temperature profile optimized for the respective powder mixture, providing for a heating rate of not more than 5 K/min, more preferably of not more than 1 to 2 K/min. In this way, the mixture to be debound is heated gently and homogeneously.

The sintering step d) of the method of the invention is not subject to any specific limitations, except for the fact that the binder has to be completely removed beforehand. It is preferred, however, to carry out the sintering step upon formation of a liquid phase, as will be described in further detail below.

The known technology of producing molded articles of aluminum alloys by powder metallurgy compression molding processes is based on the theoretical assumption that the compression process mechanically damages the surface of the alumina-covered aluminum particles in the matrix, said damage allowing for a metallurgic reaction. However, a (completely) debound brown body obtained by injection molding *de facto* is a packed bed of metal powder, the oxide skins of the metals not being subject to any mechanical load and thus not being subject to this known mechanism. This means that there are no direct metal-metal contacts between the powder particles. Nevertheless, by appropriately selecting the sintering conditions, the method of the invention succeeds in achieving the required shrinking in which the compaction of the sintered body becomes manifest, and thus succeeds in obtaining molded parts having been compacted to the greatest possible extent.

Therefore, according to the invention, embodiments are preferred in which, in step d), the completely debound brown body is sintered while forming a liquid phase. Without wishing to be bound by any theory, the inventors believe that the liquid phase, which is partly intermediary, but mainly stationary, i.e. is in a state of thermodynamic equilibrium with the solid Al phase, establishes the required contact between the metals in the powder mixture via microcracks, micropores or similar "openings" in the oxide skins of the metal powder particles and by creeping under the oxide skins, and thus it promotes the formation of a highly compacted sintered body out of the completely debound brown body. It is particularly preferred to carry out the sintering in step d) at a temperature between the solidus and the liquidus temperatures of the respective aluminum alloy, so that, at every point in time during the sintering process, a portion of the alloying metals, which can be controlled by selecting the adequate temperature profile, is in a liquid state, which efficiently prevents a loss of dimensional stability.

The composition of the respective atmospheres in the individual steps of the inventive method is not subject to any specific limitations, except for the presence of oxygen for thermal debinding in step c); those skilled in the art are capable of selecting the atmosphere which is best suited for the respective powder mixture for each step, vacuum also being an option. However, the sintering step d) is preferably carried out in an extremely dry, nitrogen-containing atmosphere, i.e. in pure nitrogen, under normal pressure or under reduced pressure ("partial pressure sintering"), or in a mixture of nitrogen and pure inert gas (helium, argon), preferably having a dew point below -40 °C, as the presence of nitrogen significantly promotes the powder particles' wettability with the developing metal melt.

The sintering step may be optionally followed by a suitable additional treatment by which the finished molded parts are kept in the desired shape. It is, for example, possible to apply the known hot isostatic pressing (HIP) process in order to achieve the desired final density of the molded parts. In this process, residual pores which are still present after the sintering step are sealed under the influence of external gas pressure and high temperatures.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a photograph of the green body (top) and of the sintered body (bottom) obtained therefrom in Example 9.

- 5 Figure 2 is a photograph of the green body (left) and the sintered body (right) obtained therefrom in Example 10.

The invention will be described in further detail below, referring to non-limiting specific exemplary embodiments.

10

EXAMPLES

- All the feedstocks produced in the examples below were homogenized in a heated laboratory compounder at 190 °C. Bars for tensile tests or hollow cylinders, respectively, were formed from these feedstocks by injection molding according to ISO 2740, applying the method of the invention as described below. A hydraulic injection molding machine (Battenfeld HM 600/130) with PIM equipment was used for producing the green bodies.

- In a first step, the feedstock was at first filled into the funnel of the injection molding machine. The injection molding process for producing the green bodies comprised the following steps: Using a heated injection cylinder with a rotating screw inside, the pretreated charging material was plastified and predosed according to preset parameters (including, for example, rotational speed, dosing volume, back pressure, etc.). Then the predosed amount was injected into an adequately tempered instrument. Depending on the feedstock and the binder used therein, the plastification temperature in the injection cylinder ranged between 120 and 220 °C, while the temperature inside the instrument was between 25 and 140 °C. After a sufficiently long cooling period, the injection molding instrument was opened and the green body was discharged from and taken out of the instrument using a handling device.

30

Example 1 – Tensile test bars: solvent debinding/thermal debinding

A commercially available metal powder mixture (Alumix® 231 from Ecka), consisting of aluminum with 14 % by weight of silicon, 2.5 % by weight of copper, and 0.6 % by weight of magnesium, was thoroughly mixed with a solvent binder consisting of wax/thermoplastic to obtain a feedstock.

5

<u>Feedstock component</u>	<u>Percentage (% by weight)</u>
Alumix 231 powder*	74.8
Solvent binder: wax proportion	14.8
10 Solvent binder: thermoplastic proportion	8.2
Stearic acid	<u>2.2</u>
	100.0

* commercially available metal powder mixture of aluminum and 14 % by weight of silicon, 2.5 % by weight of copper, and 0.6 % by weight of magnesium (from Ecka)

15

Debinding and sintering of the tensile test bars

This feedstock was first debound by solvent extraction using acetone in a 60 l oven at 45 °C in 12 h.

20

The thus obtained brown body contained approximately 14.5 % by weight of residual binder, which was subsequently removed by thermal debinding according to the invention in an atmosphere containing pure oxygen, applying a temperature profile ranging from 150 °C to 320 °C for 1 h and then from 320 to 420 °C for 1.5 h. The thus completely debound brown body was then sintered within 1 h at 560 °C in pure nitrogen (dew point: -50 °C).

25

Results

Length shrinkage: 11.6 %

30

Shrinkage of the bars' diameter: 12.25 %

Sintered density: 2.36 g/cm³

Example 2 - Tensile test bars: thermal debinding in a single step

<u>Feedstock component</u>	<u>Percentage (% by weight)</u>
Aluminum powder	67.1
5 Master alloy powder*	4.3
POM binder	25.8
Lucryl G55**	<u>2.8</u>
	100.0

10 * master alloy consisting of 50/50 aluminum and magnesium

** commercially available poly(methylmethacrylate) (PMMA; from BASF)

Debinding and sintering of the tensile test bars

Complete thermal debinding was carried out in a 40 l oven in the presence of 200 l/h

15 of pure oxygen according to the following debinding profile:

- heating to 130 °C at a heating rate of 2 K/min

- temperature maintained at 130 °C for 4 h

- heating to 200 °C at a heating rate of 2 K/min

- temperature maintained at 200 °C for 5 h

20 - heating to 420 °C at a heating rate of 2 K/min

- temperature maintained at 420 °C for 4 h

The weight lost during thermal debinding amounted to 24.2 %.

Then the bars were sintered for 1 h in pure nitrogen, the oven temperature being set

25 to 665 °C and amounting to approximately 630 °C inside the oven.

Results

Length shrinkage: 12.27 %

Shrinkage of the bars' diameter: 14.52 %

30 Sintered density: 2.46 g/cm³

Example 3 - Tensile test bars: double thermal debinding

<u>Feedstock component</u>	<u>Percentage (% by weight)</u>
Aluminum powder	70.1
5 Magnesium powder	2.2
POM binder	24.0
Surfactant*	<u>3.7</u>
	100.0

10 * ethoxylated C₁₃-C₁₅-oxoalcohol having 7 EO-units

Debinding and sintering of the tensile test bars

At first, a first thermal debinding was carried out in a 50 l oven in 500 l/h of air at 180 °C for 14 h. Weight loss: 27.0 %.

15

Thereafter, a second thermal debinding was carried out at a temperature of up to 420 °C in pure nitrogen within 1 hour, again followed by sintering for 1 h at an oven temperature set to 665 °C.

20 Results

Length shrinkage: 9.5 %

Shrinkage of the bars' diameter: 11.4 %

Sintered density: 2.13 g/cm³

Example 4 - Tensile test bars: catalytic/thermal debinding

<u>Feedstock component</u>	<u>Percentage (% by weight)</u>
Aluminum powder	70.1
5 Magnesium powder	2.2
POM binder	24.0
Surfactant*	<u>3.7</u>
	100.0

10 * ethoxylated C₁₃-C₁₅-oxoalcohol having 7 EO-units

Debinding and sintering of the tensile test bars

At first, catalytic debinding was carried out in a 50 l oven using 2 % by volume of HNO₃ in 500 l/h of nitrogen (technical grade) at 140 °C for 10 h. Weight loss: 22.1 %.

15 Thereafter, bead-like outgrowths were observed on the surface, which were assumed to have been formed by the reaction of Mg with HNO₃.

Thereafter, thermal debinding was carried out at a temperature of up to 420 °C in pure nitrogen within 1 hour, as described in Example 3, again followed by sintering
20 for 1 h at an oven temperature set to 665 °C.

Results

Length shrinkage: 10.7 %

Shrinkage of the bars' diameter: 14.65 %

25 Sintered density: 2.36 g/cm³

Example 5 - Tensile test bars: catalytic/thermal debinding

	<u>Feedstock component</u>	<u>Percentage (% by weight)</u>
	Aluminum powder	70.1
5	Magnesium powder	2.2
	POM binder	24.0
	Surfactant*	<u>3.7</u>
		100.0

10 * ethoxylated C₁₃-C₁₅-oxoalcohol having 7 EO-units

Debinding and sintering of the tensile test bars

At first, catalytic debinding according to Example 4 was carried out at 140 °C for 24 h, using 80 g anhydrous oxalic acid on a sublimation dish instead of HNO₃. Weight
15 loss: 23.0 %. When using oxalic acid, there were no outgrowths appearing on the surface. Thereafter, thermal debinding and sintering were also carried out according to Example 4.

Results

20 Length shrinkage: 14.28 %

Shrinkage of the bars' diameter: 15.68 %

Sintered density: 2.42 g/cm³

Example 6 - Tensile test bars: catalytic/thermal debinding

	<u>Feedstock component</u>	<u>Percentage (% by weight)</u>
	Alumix 231 powder*	70.8
5	POM binder*	25.6
	Surfactant**	<u>3.6</u>
		100.0

* commercially available metal powder mixture of aluminum and 14 % by weight of silicon, 2.5 % by weight of copper, and 0.6 % by weight of magnesium (from Ecka)

** ethoxylated C₁₃-C₁₅-oxoalcohol having 7 EO-units

Debinding and sintering of the tensile test bars

At first, catalytic debinding was carried out according to Example 5. Weight loss: 25.2 %. Thereafter, thermal debinding and sintering were carried out according to Example 4, applying an oven temperature set to 560 °C.

Results

Length shrinkage: 11.2 %

Shrinkage of the bars' diameter: 13.2 %

Sintered density: 2.45 g/cm³

Example 7 - Tensile test bars: catalytic/thermal debinding

<u>Feedstock component</u>	<u>Percentage (% by weight)</u>
Aluminum powder	68,0
5 Master alloy powder*	4,3
POM binder	24,0
Surfactant**	<u>3,7</u>
	100,0

10 * master alloy consisting of 50/50 aluminum and magnesium

** ethoxylated C₁₃-C₁₅-oxoalcohol having 7 EO-units

Debinding and sintering of the tensile test bars

At first, catalytic debinding was carried out according to Example 5. Weight loss:

15 23.2 %. Thereafter, thermal debinding and sintering were carried out according to Example 4.

Results

Length shrinkage: 12.6 %

20 Shrinkage of the bars' diameter: 13.25 %

Sintered density: 2.56 g/cm³

Example 8 – Hollow cylinders: catalytic/thermal debinding

<u>Feedstock component</u>	<u>Percentage (% by weight)</u>
Aluminum powder	68.0
5 Master alloy powder*	4.3
POM binder	24.0
Surfactant**	<u>3.7</u>
	100.0

10 * master alloy consisting of 50/50 aluminum and magnesium

** ethoxylated C₁₃-C₁₅-oxoalcohol having 7 EO-units

Debinding and sintering of the hollow cylinders

At first, thermal debinding was carried out according to Example 5. Weight loss:

15 23.7 %. Thereafter, thermal debinding and sintering were carried out according to Example 4.

Results

Height shrinkage: 17.24 %

20 Diameter shrinkage: 14.48 %

Sintered density: 2.59 g/cm³

Example 9 - Tensile test bars: catalytic/thermal debinding

	<u>Feedstock component</u>	<u>Percentage (% by weight)</u>
	Aluminum powder	67.1
5	Master alloy powder*	4.3
	POM binder*	25.8
	Lucryl G55**	<u>2.8</u>
		100.0

10 * master alloy consisting of 50/50 aluminum and magnesium
** commercially available poly(methylmethacrylate) (PMMA; from BASF)

Debinding and sintering of the tensile test bars

At first, catalytic debinding was carried out according to Example 5. Weight loss:
15 25.7 %. Thereafter, thermal debinding and sintering were carried out according to Example 4.

Results

Length shrinkage: 13.57 %
20 Shrinkage of the bars' diameter: 19.55 %
Sintered density: 2.59 g/cm³

Example 10 – Hollow cylinders: catalytic/thermal debinding

<u>Feedstock component</u>	<u>Percentage (% by weight)</u>
Aluminum powder	67.1
5 Master alloy powder*	4.3
POM binder	25.8
Lucryl G55**	<u>2.8</u>
	100.0

10 * master alloy consisting of 50/50 aluminum and magnesium

** commercially available poly(methylmethacrylate) (PMMA; from BASF)

Debinding and sintering of the hollow cylinders

At first, catalytic debinding was carried out according to Example 5. Weight loss:
15 25.6 %. Thereafter, thermal debinding and sintering were carried out according to Example 4.

Results

Height shrinkage: 16.52 %

20 Diameter shrinkage: 14.48 %

Sintered density: 2.56 g/cm³

25 The method of the invention is thus capable of providing sintered bodies of aluminum alloys by injection molding, which are suitable for practical applications in different fields, including the fields of transport, construction, mechanical engineering, packaging industry, iron and steel industries, electronic engineering, household appliances, etc., for example for dissipating heat as heat sinks in electronic devices, or as
30 components of air conditioning systems.

CLAIMS

1. A method for producing molded articles based on aluminum alloys by metal injection molding, comprising the following steps:

5 a) producing a feedstock by mixing the metals contained in the desired alloy in the form of metal powders and/or one or more metal alloy powders with a binder;

b) producing a green body by injection molding said feedstock;

c) producing a brown body by at least partially removing the binder from the green body by catalytic and/or solvent and/or thermal debinding;

10 d) sintering the at least partially debound brown body to obtain the desired molded article;

characterized in that, in step c), the binder is completely removed, wherein thermal debinding is carried out to remove the (residual) binder, optionally after having carried out one or more previous debinding steps, said thermal debinding being
15 carried out in an atmosphere containing at least 0.5 % by volume of oxygen, where-
after the thus obtained, completely debound brown body is sintered.

2. The method according to claim 1, characterized in that, in addition to aluminum, the aluminum alloy contains one or more metals selected from magnesium,
20 copper, silicon, and manganese.

3. The method according to claim 1 or claim 2, characterized in that, in addition to aluminum, the aluminum alloy contains one or more metals at a percentage of 0.5 to 25 % by weight, respectively.

25 4. The method according to any one of the claims 1 to 3, characterized in that the metal(s) is/are used as (a) master alloy powder(s).

5. The method according to any one of the preceding claims, characterized in
30 that a polyacetal-based binder, e.g. a polyoxymethylene (POM) binder, is used as said binder.

6. The method according to claim 5, characterized in that the binder consists of 50 to 95 % of polyacetal.

7. The method according to claim 5, characterized in that the binder consists of 80 to 90 % of polyacetal.

8. The method according to any one of the claims 1 to 7, characterized in that step c) only includes thermal debinding in the presence of oxygen, which is carried out in one or more steps and removes the entire binder.

9. The method according to any one of the claims 1 to 7, characterized in that step c) includes solvent debinding to remove the main part of the binder, followed by said thermal debinding to remove the residual binder.

10. The method according to any one of the claims 1 to 7, characterized in that step c) includes catalytic debinding to remove the main part of the binder, followed by said thermal debinding to remove the residual binder.

11. The method according to claim 10, characterized in that the catalytic debinding is carried out in the presence of at least one acid selected from nitric acid, oxalic acid, formic acid, and acetic acid.

12. The method according to claim 11, characterized in that sublimated oxalic acid is used as the acid.

13. The method according to any one of the preceding claims, characterized in that said thermal debinding to remove any residual binder is carried out at a temperature below 500 °C.

14. The method according to claim 13, characterized in that said thermal debinding to remove any residual binder is carried out applying a specific temperature profile ranging between 100 and 420 °C.

15. The method according to claim 13 or claim 14, characterized in that the heating rate during said thermal debinding process for removing the residual binder does not exceed 5 K/min.

5 16. The method according to claim 15, characterized in that the heating rate does not exceed 1 to 2 K/min.

10 17. The method according to any one of the preceding claims, characterized in that, in step d), the completely debound brown body is sintered while forming a liquid phase.

18. The method according to claim 17, characterized in that sintering is carried out at a temperature between the solidus and the liquidus temperatures of the respective aluminum alloy.

15 19. The method according to any one of the preceding claims, characterized in that the heating rate to reach the sintering temperature after said thermal debinding step ranges from 4 to 20 K/min.