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(54) A method of manufacturing objects based on aluminium.

(57) The invention relates to a method of manufacturing objects containing aluminium, by starting from aluminium and other metals in powder form, and 0.5-50 vol.% additives, mixing said starting materials, densifying them, binding the particles together and carrying out a moulding process, whereby one starts with metals in their elementary condition in which besides aluminium up to 6.0 wt.% copper, up to 3.5 wt.% magnesium, up to 1.0 wt.% silicon, up to 5.5 wt.% zinc, up to 10.0 wt.% tin, and/or up to 6.0 wt.% nickel as element in powder form has been added and a ceramic hardener in particulate form in an amount of 5-20 vol.% pre-treated by annealing-drying in order to decrease the amount of hydrogen, followed by cold isotatic compression of the mixture into billets, which are subsequently degassed and sintered, whereby said degassing and said sintering take place in one heat treatment and whereby finally the sintered product is subjected to a heat treating process and cooled.

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The invention relates to a method of manufacturing objects containing aluminium, by starting from aluminium and other metals in powder form, and 0.5-50 vol.% additives, mixing said starting materials, densifying them, binding the particles together and carrying out a moulding process.

This method is known from EP-A-0 213 113 according to which sintered molded objects have been produced from an aluminium-sinter mixture to which one added powdery adding substances having a size of 30 - 300 μm in an amount of 0.5 - 50 vol.%, which mixture is pressed to an intermediate-object, heated till the sinter temperature below the melting point of aluminium and sintered under a protecting atmosphere. As a powdery adding substance, oxides and/or silicates have been used such as glass beads or zirconium silicate. It appeared that the objects as such obtained have mechanical properties such as strength and elongation which can be improved.

According to US-A-4,569,822 one produces an aluminium comprising material for the production of substrates for a computer disc. However to the aluminium comprising starting material no hardener has been added, as according to the invention.

From US-A-4,743,299 an aluminium comprising alloy is known in which ceramic particles have been divided, which material has been used as a substrate for a semiconductor. This known material is composed from 50 - 65 vol.% aluminium or aluminium alloy and a maximum amount of about 10 vol.% binding agent and the remaining part is ceramic particles. Contrary to this according to the invention one starts with elementary aluminium and the further metallic component also is at least one metallic element. Besides this, according to this US patent degassing and sintering has been carried out in two separate steps.

From EP-A-0 240 251 a method of preparing a composite metal matrix containing aluminium, magnesium or alloys thereof and a hardener is known, wherein the hot isostatic compression takes place by charging the material to a container of pure aluminium, in which a sub-atmospheric pressure is generated in order to carry out degassing and the content of the container is heated at 550 °C at a pressure of 10^{-3} torr for 2 hours.

The object of the present invention is to obtain a more efficient method of manufacturing objects containing aluminium, which method can be carried out in a simpler and cheaper manner whilst maintaining or improving the mechanical properties of the objects obtained.

The degassing and compression in an aluminium container is a frequently used method which is known per se, which method is inter alia also known from US Patents 4,946,500 and 4,933,007. The container used thereby is made of soft aluminium or an alloy thereof (canning material), which is removed from the semimanufactured product (a bar or a billet) after processing. The method according to the invention does not use such a canning process.

The method according to the invention is characterized in that one starts with metals in their elementary condition in which besides aluminium up to 6.0 wt.% copper, up to 3.5 wt.% magnesium, up to 1.0 wt.% silicon, up to 5.5 wt.% zinc, up to 10.0 wt.% tin, and/or up to 6.0 wt.% nickel as element in powder form has been added and a ceramic hardener in particulate form in an amount of 5-20 vol.% pre-treated by annealing-drying in order to decrease the amount of hydrogen, followed by cold isotatic compression of the mixture into billets, which are subsequently degassed and sintered, whereby said degassing and said sintering take place in one heat treatment and whereby finally the sintered product is subjected to a heat treating process and cooled.

Preferably one starts with elementary aluminium in powder form and furthermore one or moer of the following elements in powder form: up to 6.0 wt.% copper, preferably 0.1 - 6.0 wt.% copper, up to 3.5 wt.% magnesium, preferably 0.5 - 3.5 wt.% magnesium, up to 1.0 wt.% silicon, preferably 0.2 - 1.0 wt.% silicon, up to 5.5 wt.% zinc, preferably 3.0 - 5.5 wt.% zinc, up to 10.0 wt.% tin, preferably 5.0 - 10.0 wt.% tin and/or up to 6.0 wt.% nickel, preferably 0.1 - 6.0 wt.% nickel.

Preferably SiC in powder form or Al_2O_3 in powder form or fibrous Al_2O_3 is used as the hardener. Furthermore it is preferred that the ceramic hardener is pre-treated by annealing-drying at 550 - 650 °C in an inert atmosphere for 1 - 4 hours.

According to the invention said degassing-sintering is carried out in one step in an atmosphere preferably consisting of argon and/or nitrogen, by heating at a rate of 2 - 6 °C/min and sintering at 580-640 °C for 30 - 90 minutes.

The invention will be explained in more detail in the following description, wherein reference is made to the appended drawings, in which:

Figure 1 shows the evolution of hydrogen and moisture during the pre-heating of Al_2O_3 fibres from room temperature to 600 °C;

Figure 2 shows the degassing-sintering cycle according to the present invention; and

Figure 3 shows the evolution of hydrogen and moisture during the degassing-sintering cycle of billets consisting of Al-4.5 Cu, 0.7 Si, 0.5 Mg-10 (per cent by volume) SiC (powder).

The hardener in particulate form, such as SiC, powdered or fibrous Al_2O_3 or Si_3N_4, is subjected to an annealing-drying process prior to mixing the hardener with the elementary metal in powder form. Said annealing-drying process is carried out at a temperature of 550 - 650 °C for 1 - 4 hours, in an atmosphere containing argon and/or nitrogen, followed by quick cooling in the air whilst flushing with nitrogen. Said annealing-drying process is carried out in order to remove any moisture and hydrogen included at the surface of the ceramic hardener. The upper limit of 650 °C has been selected because the subsequent sintering takes place at a temperature of up to about 650 °C. If said hydrogen is not removed it will cause problems during the subsequent sintering process, resulting in a weakening of the interface between the metal matrix and the ceramic hardener, blistering at the surface and internal porosity of the extruded product. The inert atmosphere of nitrogen and/or argon is used in order to prevent the readsorption of moisture during the cooling process in the air and the subsequent mixing.

Specific examples of the matrix compositions are:

Al - (4.0 - 6.0) Cu - (0.5 - 1.0) Mg - (0.5 - 1.0) Si
Al - (0.1 - 0.5) Cu - (1.0 - 1.5) Mg - (0.2 - 0.5) Si
Al - (0.5 - 1.5) Cu - (1.0 - 3.5) Mg - (0.5 - 5.5) Zn
Al - (1.0 - 2.0) Cu - (7.0 - 10) Sn - (0.5 - 1.0) Ni

According to the invention the metals are used as powdered metals in elementary condition, because they are 5 - 15 times as cheap as the alloys of the desired metal compounds, obtained by pulverizing or by grinding techniques while supplying a great deal of energy. In addition to that said elementary metals in powder form are more easily compressed and sintered than the alloys in powder form. Preferably the particle size of the elementary powders is less than 200 µm, with an average particle size close to that of ceramic particles, namely 25 µm. The elementary powders and the hardeners in powder form are mixed in a mixer of the "turbula" type. The compound containing a hardener in the form of short fibres is dry mixed in a ball mill. The amount of hardener in particulate form varies from 5 to 20%, whilst an amount of 10 vol.% is preferred for compounds having a certain resistance to wear.

After mixing the mixture composed is subjected to cold isostatic compression, in order to obtain billets having a density of 75 - 85% of the theoretic density. A density like this facilitates an optimum attunement between the "green" strength necessary for processing the billets and the subsequent degassing.

After said cold isostatic compression, which is preferably carried out at room temperature and a pressure of 80 - 250 MPa, the billets are degassed and sintered in a combined cycle, in a protecting atmosphere of argon and/or nitrogen. It is not necessary to use a vacuum or canning thereby. The degassing is according to the invention incorporated in the sintering cycle, because according to the invention it is necessary to limit the presence of gases, in particular hydrogen, in the billet. When the gases are not removed, the properties of the compound may be affected, as a result of which the compound may for example exhibit blistering after being subjected to the subsequent heat treatment or during the processing of the billets at an elevated temperature.

The sintering of the elements in powder form, whereby a liquid phase is formed, takes place in order to achieve that a matrix of an alloy is formed within a short period of time as a result of the quick transport of the atoms through the liquid phase. During the formation of the liquid phase the thin but highly stable oxide film, which is always present on the surface of the aluminium particles, is disturbed and a good binding of the particles is obtained as a result of the subsequent necking, whereby the liquid phase facilitates the transport of materials. This liquid phase also makes it easier to obtain an excellent quality of the interface between the metal matrix and the ceramic hardener. A eutectic liquid phase is formed as a result of the reaction of aluminium with elements in powder form, such as Cu, Mg, Si, Zn and Sn. The development of hydrogen takes place during the heating of the billet from room temperature to the sintering temperature, which varies between 580 °C and 640 °C, dependent on the composition of the alloy. The rate at which heating takes place varies from 2 - 6 °C/min, and sintering is carried out for a period of 30 - 90 minutes, depending on the degree of homogenization, the formation of the matrix alloy and depending on the dimensions of the billets. The method is carried out in ovens normally used for homogenizing billets, before the extrusion takes place. After sintering the billet is cooled down to a temperature of 20 - 30 °C, possibly outside the oven in the air, or to extrusion temperature, when said extrusion takes place contiguous to sintering. During said cooling the billets are washed with nitrogen, in order to prevent the absorption of water vapour. As a result of the combined cycle of degassing-sintering in a protecting atmosphere billets of a homogeneous matrix alloy having a well-defined interface between the matrix and the hardener and having a very low hydrogen content is produced, so that the amount of hydrogen that may be present does not affect the final products. The billets thus obtained may then be processed further into structural objects by extruding, forging, rolling, drawing and other operations which are normally carried out on metals. By using the method according to the invention such products are obtained in a cheaper and more efficient manner. From this semi-product one can produce especially toothed wheels, conducting rails for copying apparatus and printers.

The invention will be further explained below by means of the following examples, which are in no way to be considered limitative.

Examples I - III

In the three examples the hardener was powdered SiC (1), powdered Al_2O_3 (2) and fibrous Al_2O_3 (3). These hardeners were first dried by annealing at 600 °C for 3.5 hours, in order to evolute the entrapped hydrogen. Table A lists the hydrogen content of the hardener before and after annealing (ppm = volume/weight)

TABLE A

hydrogen content of hardener before and after annealing (ppm)			
	hardener		
	powdered SiC	powdered Al_2O_3	fibrous Al_2O_3
before annealing	200	240	1900
after annealing	10	12	15

After annealing this hardener was mixed, in an amount of 10 vol.%, with elements in powder form, such as aluminium, 4.5 wt.% Cu, 0.5 wt.% Mg and 0.7 wt.% Si.

The mixture was subjected to cold isostatic compression at ambient temperature, whereby "green" billets having a theoretic density of 80% were obtained. These billets were degassed-sintered in a nitrogen atmosphere, according to the time and temperature curves of Figure 2. Said degassing-sintering was carried out in a nitrogen atmosphere. During degassing heating took place with a temperature increase of 6 °C/min. Sintering took place at a temperature of 590 °C for a period of 60 minutes. After sintering the billets were quickly cooled at a rate of about 25 °C/min, whereby the billets were flushed with nitrogen. The hydrogen content of the sintered billets is very low, as shown in Table B, which points to a very effective degassing-sintering cycle. Figure 3 graphically illustrates the dependence of the hydrogen/water vapour developed on the temperature used in the degassing-sintering process. Table B lists the hydrogen content of the three different billets before and after degassing-sintering, whereby the billets contain 10 vol.% of powdered SiC, powdered Al_2O_3 and fibrous Al_2O_3 respectively, with the following composition of the elementary metals: Al-4.5 wt.% Cu, 0.5 wt.% Mg, 0.7 wt.% Si. The hydrogen content is expressed in ppm.

TABLE B

hydrogen content (ppm)			
billet	hardener 10 vol.%		
	powdered SiC	powdered Al_2O_3	fibrous Al_2O_3
before degassing-sintering	2,5	2,6	2,9
after degassing-sintering	0,8	0,8	1,0

The sintered billets exhibit a fine homogeneous micro-structure for the matrix and a homogeneous distribution of the hardener, as became apparent from photographs made by means of a microscope. For comparison a material (20 wt.% Si, 3 wt.% Cu and 1 wt.% Mg) was made from pre-alloyed atomised aluminium in powder form and 10 vol.% SiC in powder form, so that a compound being resistant to wear was obtained. The following successive processing steps were thereby carried out in accordance with the known state of the art, viz. mixing, compressing, canning, degassing at a reduced pressure and extruding. This matrix, which is formed of a previously formed alloy containing 10 vol.% SiC as a hardener, is known to have very good mechanical properties, such as strength, extension and Youngs modulus, and measurements carried out have shown that the material obtained in accordance with the invention has good mechanical properties comparable therewith, whilst on the other hand the method according to the invention can be carried out in a simpler, more efficient and therefore cheaper manner.

Claims

1. A method of manufacturing objects containing aluminium, by starting from aluminium and other metals in powder form, and 0.5-50 vol.% additives, mixing said starting materials, densifying them, binding the particles together and carrying out a moulding process, characterized in that one starts with metals in their elementary condition in which besides aluminium up to 6.0 wt.% copper, up to 3.5 wt.% magnesium, up to 1.0 wt.% silicon, up to 5.5 wt.% zinc, up to 10.0 wt.% tin, and/or up to 6.0 wt.% nickel as element in powder form has been added and a ceramic hardener in particulate form in an amount of 5-20 vol.% pre-treated by annealing-drying in order to decrease the amount of hydrogen, followed by cold isotatic compression of the mixture into billets, which are subsequently degassed and sintered, whereby said degassing and said sintering take place in one heat treatment and whereby finally the sintered product is subjected to a heat treating process and cooled.

2. A method according to claim 1, characterized in that one or more of the elements in powder form are 0.1 - 6.0 wt.% copper, 0.5 - 3.5 wt.% magnesium, 0.2 - 1.0 wt.% silicon, 3.0 - 5.5 wt.% zinc, 5.0 - 10 wt.% tin and/or 0.1- 6.0 wt.% nickel.

3. A method according to claim 1, characterized in that the hardener used is SiC or Al_2O_3 in powder form or fibrous Al_2O_3.

4. A method according to claims 1 - 3, characterized in that said ceramic hardener is pre-treated by annealing-drying at 550 - 650 °C in an inert atmosphere for 1 - 4 hours.

5. A method according to claims 1-4, characterized in that the precompressed billets are degassed and sintered at a normal pressure.

6. A method according to claims 1-5, characterized in that said degassing-sintering is carried out in an atmosphere of argon and/or nitrogen, by heating at a rate of 2 - 6 °C/min and sintering at 580 - 640 °C for 30 - 90 minutes.

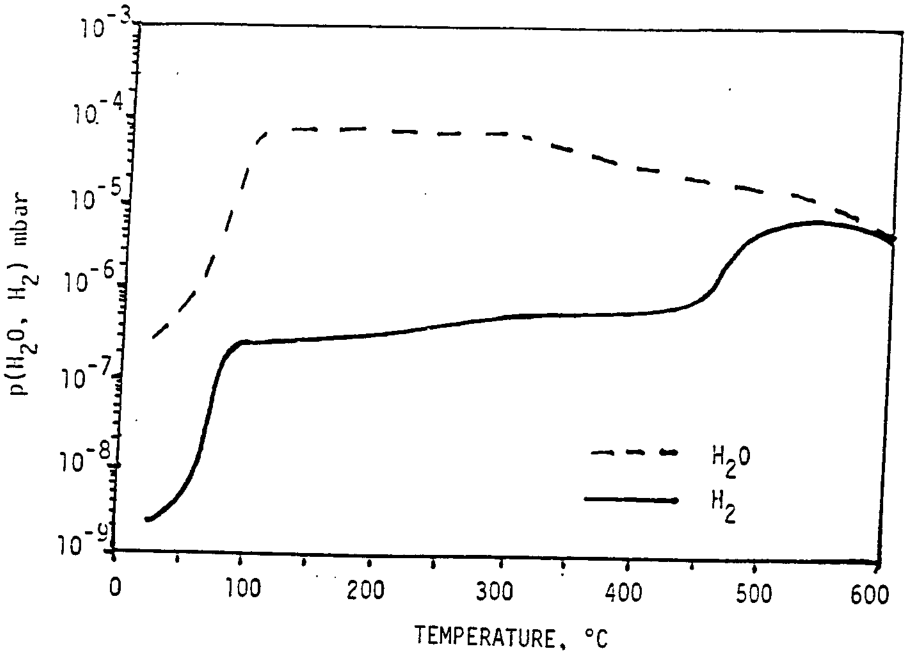
10^-3
10^-4
10^-5
10^-6
10^-7
10^-8
10^-9
p(H2O, H2) mbar
H2O
H2
0
100
200
300
400
500
600
TEMPERATURE, °C

Fig. 1

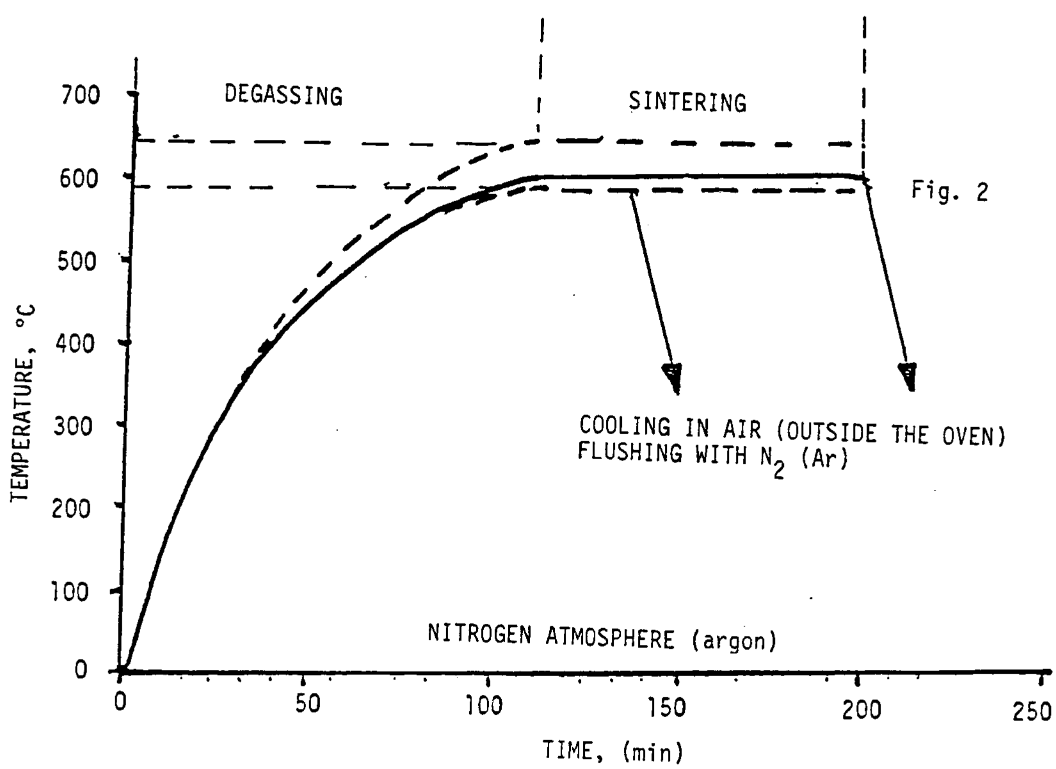
DEGASSING
SINTERING
700
600
500
400
300
200
100
0
TEMPERATURE, °C
COOLING IN AIR (OUTSIDE THE OVEN)
FLUSHING WITH N2 (Ar)
NITROGEN ATMOSPHERE (argon)
0
50
100
150
200
250
TIME, (min)

Fig. 2

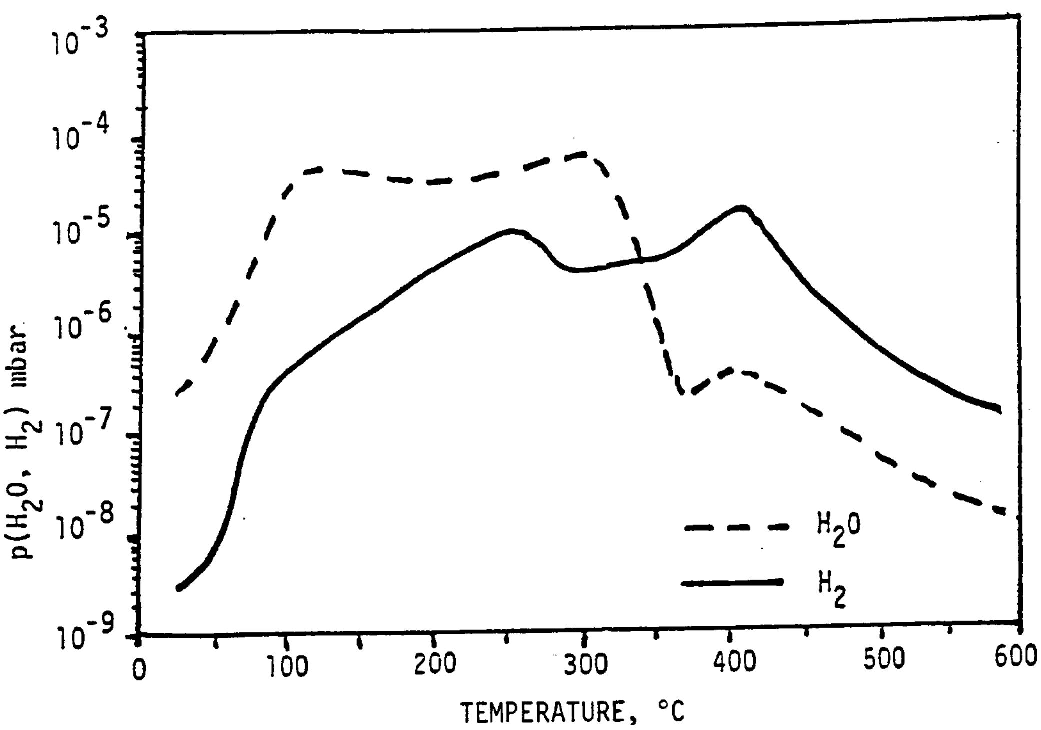
10-3
10-4
10-5
10-6
10-7
10-8
10-9
p(H2O, H2) mbar
0
100
200
300
400
500
600
TEMPERATURE, °C
H2O
H2

Fig. 3

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 20 2681

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
Y	US-A-4 569 822 (S.W.BROWN) * column 4, line 16 - line 29 * * column 4, line 3 - line 15 * * column 4, line 64 - column 5, line 10; claims 1,6,12,14 * ---	1-6	B22F1/00 C22C32/00 C22C1/05
Y	US-A-4 743 299 (M.J.PRIOR ET AL) * column 6, line 48 - column 7, line 27; claims 1-3 * ---	1-6	
A	EP-A-0 213 113 (MIBA) * example 4 * ---	1-6	
A	EP-A-0 410 417 (UBE INDUSTRIES) * page 3, line 30 - page 4, line 20 * * page 5, line 50 - line 58 * ---	1-6	
A	FR-A-2 607 741 (PECHINEY) * page 4, line 33 - page 6, line 7; claims 1-3 * ---	1-6	TECHNICAL FIELDS SEARCHED (Int.Cl.5)
A	DATABASE WPI Section Ch, Week 9211, Derwent Publications Ltd., London, GB; Class M22, AN 92-085195 & JP-A-4 028 471 (SUZUKI MOTOR CORP) 31 January 1992 * abstract * -----	1	B22F C22C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23 December 1993	Schruers, H

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

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