

Process and apparatus for vacuum distillation of high-purity magnesium

The invention relates to a process for producing high-purity magnesium by means of distillation at reduced pressure, and to apparatuses for performing the process.

Magnesium has a low boiling point compared with most other metals and this is why many processes for the recovery of the raw metal or also for the recycling of magnesium from scrap metal are performed via the process step of vacuum distillation, since a magnesium that is largely purified from less volatile metals can be recovered in this way in a single step. If it is also sought to remove these volatile substances in order to produce high-purity magnesium, for example as is desirable for the semiconductor industry, vacuum distillation facilities having a plurality of condensation regions arranged in series are used, and therefore high-purity fractions, in which the impurities are merely in the ppm range, are also obtained from a number of fractions contaminated to a significant extent by other volatile metals, such as zinc and cadmium. Such a process is described in EP 1 335 030 A1, wherein the steam rising from a crucible containing an impure magnesium melt is conveyed via a multiplicity of successive deposition plates heated to decreasing temperatures and deposits on these plates in fractionated form.

The evaporation temperature of magnesium can be lowered with reduction of pressure until below the temperature of the melting point, and a particular feature of this metal is that its steam pressure even below the melting point is still so high that it is sufficient for a technically useful resublimation of high-purity magnesium crystals. Accordingly, most known vacuum distillation processes in accordance with the prior art for producing high-purity magnesium lead to the deposition of solid magnesium crystals.

Such magnesium crystals, in view of their low content of foreign elements, are indeed referred to as high-purity in the chemical sense, but the crystals have a high surface/volume ratio, and, when such crystals are remelted for the purpose of producing a semifinished product or near-net-shape articles, the oxide skins originally present on the surface of the magnesium crystals due to the high reactivity are distributed as non-metal inclusions in the melt and remain in the solidified material. Although they have only low

concentration values, such inclusions, however, can adversely influence the corrosion behaviour of the otherwise high-purity magnesium, for example.

In accordance with EP 1 335 032 A1, there is a process in which an impure magnesium melt is evaporated in an evaporation vessel from high-purity graphite, wherein this steam then precipitates as liquid melt in a condensation crucible likewise consisting of graphite. Both crucibles are surrounded by a bell made of graphite, which prevents the magnesium steam from coming into contact with the cold wall of the vacuum retort surrounding the bell and condensing there. In order to bring both the evaporation crucible and the condensation crucible to the temperatures necessary for the process and simultaneously to keep the retort cold, two heating elements are present in the gap between the retort wall and the graphite bell. In particular due to the mounting of the heating elements within the vacuum region and the protection of the actual evaporation zone and condensation zone by the graphite bell, an increased structural outlay is created and in addition the inner volume has to be evacuated through leaks of the graphite bell, whereby magnesium steam can also pass externally at these points to the heating elements and the cold retort wall.

In contrast to most processes according to the prior art, the high-purity magnesium condenses in the liquid state in the process according to the invention, wherein a high-purity magnesium melt free from non-metal inclusions results, which forms a compact block following solidification, which is suitable for example in the sense of a semifinished product as starting material for shaping processes, without the material containing relatively large quantities of non-metal inclusions, which on the one hand can negatively influence the mechanical properties and on the other hand can negatively influence the corrosion behaviour.

In particular compared with the process cited further above in accordance with EP 1 335 032 A1, the process has the advantage that the retort can be heated externally, wherein the magnesium steam can come into contact with the inner wall of the retort without difficulty, since this wall is at such a high temperature that solid magnesium crystals cannot be deposited thereon. Likewise, the retort wall may also consist of a material that is soluble to a low extent in the magnesium melt, whereby the magnesium

melt is contaminated. A condition of this, however, is that the retort must consist of a material that releases no volatile impurities into the magnesium steam.

Due to the possibility of arranging the heating system outside the retort and also allowing the contact with the hot inner wall of the retort, which only slightly contaminates the magnesium melt, a process is created that is particularly simple and cost-effective in terms of structure compared with the prior art.

The process according to the invention will be explained hereinafter on the basis of three apparatus examples.

Fig. 1 shows a diagram of an apparatus according to the invention having the features essential to the invention in accordance with the teaching of the independent patent claim.

Fig. 2 shows a cross section through an exemplary apparatus for producing high-purity magnesium.

Fig. 3 shows a cross section through a further exemplary apparatus for producing high-purity magnesium.

In figure 1 the elements of the first apparatus example are illustrated purposefully in geometrically simple form in order to emphasize the fact that the central inventive concept is based less on the specific form of these parts, but more on the functionality of these parts in conjunction with the temperature distribution within the retort. The starting material 2 in the form of a magnesium-containing metal melt is present together with the upper region 32 of a condensation vessel 3, preferably made of a high-purity graphite, in the upper region 11 of a retort 1 produced for example from stainless steel and having an arbitrary cross section, wherein a cylindrical cross section is most favourable in practice. The upper region 11 of the retort is brought by a heating element 5 surrounding it, for example in the form of a resistance furnace, to a temperature above the boiling point of the magnesium, within the limits of the level lines 8 and 81, and is then held constant, such that steam rises

from the boiling magnesium-containing metal melt 2 in accordance with the arrows 91 and fills the interior of the upper region 11 of the retort 1, wherein it can also condense into liquid above the level line 81 and then flows back downwards again into the melt 2. Since stainless steel reacts slightly with liquid magnesium, the magnesium melt is contaminated by the alloy elements of the stainless steel upon contact therewith, however, since these elements have an irregularly lower steam pressure compared with magnesium, this contamination is not noticeable in the steam.

In order to prevent contaminated melt that drops from the region above the level line from reaching the opening 31 of the condensation vessel 3, this is protected by a cover 4, selectively also consisting of graphite, which conveys the impure magnesium back again into the melt 2. The cover 4 can be supported here directly on the upper region 32 of the condensation vessel 3 or can also be connected laterally or from above to the inner wall of the retort. In any case however, the fastening has to be formed such that the cover can be removed temporarily without difficulty in order to remove the solidified high-purity magnesium 21 from the condensation vessel 3.

The melt of the magnesium-containing starting material 2 is in direct contact with the outer surface of the condensation vessel 3 in the region 32 during the distillation process in the case of this apparatus example. Since, at the end of the distillation process, practically all starting material is evaporated, the condensation vessel is empty again. Any melt that has infiltrated into the gap between the region 31 of the condensation vessel and the region 12 of the retort is irrelevant here, since the condensation vessel does not necessarily have to be removed from the retort in order to remove the solidified magnesium. The steam infiltrating into the upper region 32 of the graphite crucible in accordance with the arrow 92 condenses below the level line 8 and collects as high-purity melt 21 in the lower region 33 of the graphite crucible. In order to prevent a boiling of this high-purity melt 21, a minimum pressure can be maintained within the retort by means of an inert gas, for example argon, which brings the boiling point of the magnesium above the temperature prevailing in the region 33. Here, the temperature profile in particular of the lower part 33 of the condensation vessel 3 is determined by a separately adjustable heating element 51.

Via a barrier unit 6, for example in the form of a disc valve, which is pressed against a seat 62, for example in the form of a ceramic or graphite felt packing, via an externally actuatable push rod 61 that can be displaced through a vacuum feedthrough, the retort 1 can be connected to the supply chamber 13 upon movement of the push rod 61 in the direction of the arrow 93. Here, the barrier unit 6 with the valve disc and the seat 62 is present in the current example together with the upper region 11 of the retort 1 above the level line 81, that is to say at a temperature above the melting point of magnesium, such that solid magnesium cannot be deposited in the region of the barrier unit, whereby the function thereof is ensured.

The supply chamber 13, in its colder region above the level line 82, which symbolises the isotherm of the melting point, has a cover 14, preferably in the form of a removable vacuum flange, which has a number of connections besides the vacuum feedthrough 63. Here, one connection leads via a line 71 and a valve 72 to a vacuum pump 73, a further connection leads via a line 74 to a vacuum measuring instrument 75, and a third connection leads via a line 76, a valve 77 and a pressure and/or flow regulator 78 to an inert gas source 79, for example in the form of an argon pressure cylinder.

Once the retort 1 has been evacuated via the supply chamber 13 and then brought to the temperatures necessary for the distillation process, the barrier unit 6 is then opened only for a short period for the purpose of pressure adjustment and pressure correction so as to avoid excessive condensation of magnesium steam in the supply chamber 13. The duration of the closed periods is dependent here on the rise of pressure during the closed periods. In the ideal case, with sufficient degassing of highly gas-releasing parts, for example consisting of a graphite of low quality, or with use of parts made of high-purity graphite, the barrier unit 6 can remain closed for a long period of time and is only opened briefly at long intervals for the purpose of pressure monitoring. If the pressure in the meantime rises above an upper setpoint value, whereby the evaporation process of the starting material 2 is hindered, the retort 1 can be connected to the vacuum pump 73, by opening the valve 72, until the pressure has reduced again into the setpoint range. If, however, the pressure has fallen below the setpoint range, whereby there is a risk of evaporation of the high-purity magnesium melt present in the lower region 33 of the condensation vessel 3, the retort 1 is

connected to the inert gas source 79 via the flow and/or pressure regulator 78 by opening the valve 77 until the pressure has risen again into the setpoint range. In both cases the barrier unit 6 is closed immediately once the setpoint pressure range has been reached in order to prevent excess infiltration of magnesium steam into the supply chamber 31.

As soon as the distillation process in accordance with the apparatus example of image 1 is finished and the retort 1 is cooled with its contents to room temperature, the retort can be opened, for example by a sawn cut along the dashed level line 83, whereupon the high-purity magnesium 21 present in the lower region 33 of the condensation vessel 3 can be removed from the crucible following removal of the cover 4, for example by turning the entire apparatus on its head. New starting material 2 can be introduced through the opening into the evaporation region 111 of the retort in a similar manner. Then, the retort 1 has to be joined together again to the supply chamber 13 in a vacuum-tight manner, for example by means of a welding or soldering process.

The heating elements 5 and 51 used in this example according to figure 1 are resistance heating elements controlled to constant temperatures, which are located at points of the retort relevant for the distillation process, that is to say for example in the region of the upper region of the retort contacted by the melt of the starting material in order to adjust the temperature of the evaporation process, and in the lower region 33 of the condensation vessel 3 and the immediate environment of the barrier unit 6 in order to check whether the temperature in these regions is above the melting point of magnesium. Instead of the resistance heating elements 5 and 51, two induction coils or a single induction coil wound in accordance with the temperature distribution can of course also be provided, which heat the retort and/or the materials present therein.

Figure 2 shows an example of an apparatus according to the invention that is particularly suitable for rational operation under industrial conditions, wherein like numbers denote parts having the same function as in figure 1. Here, the retort 1 is welded together as central symmetrical tubular body to an upper region 11 of larger diameter and to a lower region 12 of smaller diameter consisting of a superalloy, wherein the lower region 12 extends in a tubular extension 15 into the upper region 11 of the retort. The melt of the

starting material 2 is thus present in an annular crucible, of which the side walls are formed by the wall region 111 of the upper region 11 of the retort 1 and the tubular extension 15, such that the melt does not come into contact with the outer wall of the condensation vessel.

In this example of the apparatus according to the invention, the tubular extension 15 and the lower region 12 of the retort have, internally, an inner wall with continuous conicity, such that the condensation vessel 3 in the form of a crucible consisting of high-purity graphite, which has a corresponding conicity of the outer lateral surface, does not provide a gap for the infiltration of condensing magnesium melt. In contrast to the apparatus example according to figure 1, where the condensation vessel 3 has a cylindrical inner bore, since the solidified pure magnesium block can generally be easily removed as a result of the large shrinkage, the condensation vessel 3 in the present apparatus example also has a conical inner face, such that the high-purity magnesium block 21 can be removed even more easily following solidification.

The opening 31 in the condensation vessel 3 is covered by a roof-shaped graphite cover 41 with radial bores leading upwardly at an incline for the entry of the magnesium steam according to arrow 92. The cover 41 can also be formed in a manner more complex than that in the figure, for example by also placing lateral screens in front of the radial bores, such that no splashes of the fiercely boiling melt of the starting material 2 can be flung directly into the condensation vessel 3.

The barrier unit is configured here in the form of a conical metal stopper 64, which seals with respect to the conical seat 113 of the intermediate wall 112. This sealing process is also assisted by the fact that liquid magnesium condenses in the seal gap between the metal stopper 64 and the seat 113 and prevents the passage of magnesium steam. The push rod 61, by means of which the barrier unit can be closed in the direction of the arrow 92, is actuated externally through a vacuum feedthrough 63 with ring seal 631, wherein this can be performed manually or automatically via a control pulse. Instead of the ring seal 631, the push rod 61 could also be introduced through the flange 14 into the supply chamber 13

in a sealing manner, for example by means of a metal bellow. The flange 14 is sealed in the example by means of a ring seal 141 with respect to the cylindrical supply chamber 13.

The lines 71, 74 and 76 lead, as in the previous example, to a vacuum pump 73, a vacuum measuring instrument 75 and selectively to an inert gas source, however electrically actuatable valves 72 and 77 are used here, and therefore, besides the barrier unit 64 for connecting the retort 1 to the supply chamber 13, the pressure can also be reduced and increased automatically in the direction of a setpoint pressure range in the sense described with the previous example within the scope of a control circuit.

In contrast to the previous example, only the upper region 11 of the retort 1 is heated in this apparatus with a heating element 5, for example in the form of a tubular resistance heating furnace, whereas the lower region 12 is surrounded by an insulation layer 52, which is dimensioned such that the heat passing from the upper region by means of thermal conduction through the retort wall 12 and the wall 32 of the condensation vessel as well as the downwardly travelling heat caused by the condensation of the magnesium steam, in combination with the cooling effect of the region of the retort wall 12 not insulated at the bottom, holds the temperature of the condensed high-purity magnesium melt in the desired range between the melting temperature and the boiling temperature. The temperature profile within the retort 1 can also be changed as desired within a certain range by shifting the retort in the vertical direction with respect to the furnace and insulation.

The temperature of the high-purity magnesium melt 21 can be controlled via a temperature sensor 53, for example a jacket thermocouple of type K or J, which extends via a protuberance of the wall 12 into the foot of the lower region 32 of the condensation vessel 3, and, where applicable, can be controlled such that it does not fall below the melting point of the magnesium. The moment at which the last residue of the starting material is evaporated can be determined by means of a second temperature sensor 54, for example likewise a jacket thermocouple, which measures the temperature within the melt of the starting material 2 via a protuberance of the wall of the region 111 of the retort. At this moment, where the cooling effect of the evaporation process ceases, there is specifically a sudden increase of the temperature of this thermocouple. The third temperature sensor 55

sits tightly above the barrier unit 64 in a protuberance of the lower region of the wall of the supply chamber 13 and makes it possible to check whether this barrier unit is above the temperature of the melting point of magnesium, since only then is the correct function of this barrier unit ensured. At the end of a furnace cycle, that is to say prior to the cooling of the facility, the barrier unit 64 should be lifted from the seat face 113 so that it is not soldered thereto.

In the first example of an apparatus, a variant of the heating system with two independent heating elements is presented, but in the present second example the upper retort region is heated by means of a heating element 5, wherein the lower region 12 surrounded by the thermal insulation is also heated indirectly by the upper region, wherein the heat introduced by the condensation of the magnesium steam also contributes. In the sense of the process according to the invention, apparatuses having a plurality of furnaces arranged in succession in the vertical direction are also possible, such that the upper and the lower part of the retort and additionally also the region of the barrier unit 6 can be controlled separately in each case to their specific temperature by means of a dedicated heating element.

Figure 3 shows a third example of an apparatus according to the invention, which is largely similar to the apparatus shown in figure 2. In contrast to this apparatus shown there, however, the condensation vessel 3 in the present example has a cylindrical outer face, whereby an annular gap is produced between this outer face and the inner lateral surface of the lower region 12 of the retort 1. By removing a selectively water-cooled flange 15, the crucible can be removed downwardly from the retort. In order to prevent magnesium steam from infiltrating into this gap and condensing into liquid in its lower region or into solid below the crucible base 34, this flange 15 has a feed line 761 with a flow regulation element 781, through which gas originating from an inert gas source can be introduced into the space beneath the base 34 of the condensation vessel 3. The quantity of the fed inert gas is such here that its speed in the gap outside the condensation vessel 3 is so high that it exceeds the diffusion rate of the magnesium steam potentially ready for migration in the opposite direction. As a result of this addition of inert gas, the pressure rise within the retort is indeed accelerated, whereby the intervals within which the barrier unit 64 has to be

opened for the purpose of pressure control and regulation are somewhat shorter, however this reduction is insignificant, since only small quantities of inert gas are necessary to keep the gap free.

The figures do not show the control circuits and mechanisms that are necessary to keep constant the temperatures and the pressure of the apparatuses, since their functioning, apart from the accuracy necessary for the execution of the process, is insignificant for the execution of the process.

List of reference signs

- 1 retort, generally
- 11 upper region of retort
- 111 region of 11 in contact with starting material
- 112 intermediate wall of 11 and 13
- 113 conical seat for 64 in 112
- 114 protuberance of the retort wall as protection for temperature sensor 54
- 12 lower tapered region of retort
- 121 protuberance of the supply chamber wall as protection for temperature sensor 53
- 13 supply chamber
- 131 protuberance of the retort wall as protection for temperature sensor 55
- 14 vacuum flange
- 141 ring seal
- 15 vacuum flange
- 151 ring seal

- 2 magnesium-containing metal starting melt
- 21 high-purity magnesium melt

- 3 condensation vessel, generally
- 31 opening in condensation crucible
- 32 upper zone of condensation crucible
- 33 lower zone of condensation crucible

- 4 cover
- 41 cover with lateral openings

- 5 heating system for region 11
- 51 heating system for region 12
- 52 insulation for region 12
- 53 temperature sensor in base zone of condensation vessel

- 531 protective pipe for temperature sensor
- 54 temperature sensor for evaporation zone
- 55 temperature sensor for region of barrier unit 64

- 6 barrier unit
- 61 push rod of barrier unit
- 62 seal seat for barrier unit
- 63 vacuum feedthrough for push rod
- 631 ring seal
- 64 barrier unit with conical seat

- 71 connection line to vacuum pump
- 72 barrier unit to vacuum pump
- 73 vacuum pump
- 74 connection line to vacuum measuring instrument
- 75 vacuum measuring instrument
- 76 connection line to barrier unit
- 761 connection line to flow regulator for inert gas
- 77 barrier unit
- 78 flow regulator for inert gas
- 781 flow regulator for inert gas
- 79 inert gas source

- 8 lower level limit for temperature range above boiling point
- 81 upper level limit for temperature range above boiling point
- 82 upper level limit for temperature range above melting point
- 83 level line of possible sawn cut

- 91 arrow, steam generation
- 92 arrow, steam entry into condensation vessel
- 93 arrow, lifting direction of barrier unit 6

Patent Claims

1. A process for producing high-purity magnesium by distillation at reduced pressure, characterised in that a starting material in the form of a magnesium-containing metal melt with the upper region of a crucible-shaped condensation vessel, which is formed from a material inert with respect to magnesium and which has an opening that provides protection against ingress of contaminated refluxing magnesium melt by a cover inert with respect to magnesium and that allows the entry of magnesium steam, in the upper part of a vacuum-tight retort which can be externally heated to different temperatures by one or more heating elements in the horizontal direction and which is made of a material that is largely inert with respect to magnesium or at least does not release impurities capable of evaporation is at a temperature above the melting point and in the immediate region of the magnesium-containing melt and the opening of the crucible-shaped condensation vessel is above the boiling point of magnesium, wherein the lower region of the crucible-shaped condensation vessel in a tapering region of the retort, closely surrounding the lower region of said condensation vessel, is in a temperature gradient between the boiling point and melting point of magnesium, and in that the retort can be connected at least temporarily via a barrier unit to a supply chamber, which in turn can be connected via lines and a valve to a vacuum pump, via a further line to a vacuum measuring instrument, and via a third line and a valve to an inert gas source, wherein the pressure within the retort during the distillation process is held in a setpoint pressure range, that is to say is reduced on the one hand to such an extent that the boiling point of the magnesium reduces to a temperature that is thermally sustainable for the material of the retort and on the other hand is held by selective addition of inert gas at a minimum value, at which the boiling point of the pure magnesium melt present in the lower region of the crucible-like condensation vessel is not exceeded.
2. The process according to Claim 1, characterised in that the barrier unit, for the purpose of pressure balancing between the retort and the supply chamber, is opened at intervals, whereupon the pressure detected by the vacuum measuring instrument and converted by a converter into an electric signal, after comparison with a setpoint

pressure range via a control circuit, connects the retort either via an electrically actuatable valve to the vacuum pump or via another electrically actuatable valve to an inert gas source, until the setpoint pressure range is reached, wherein the magnitude of the pressure change implemented during the last closed period of the barrier unit selectively determines the duration of the next closed period.

3. The process according to Claim 1, selectively in combination with Claim 2, characterised in that inert gas is introduced into the gap between the inner lateral surface of the lower region of the retort and the outer lateral surface of the lower region of the crucible-like condensation vessel via a needle valve in a flow quantity that prevents magnesium steam and/or magnesium melt from infiltrating into this gap.
4. The apparatus according to Claim 1, selectively in combination with Claim 2 and/or 3, characterised in that a starting material in the form of a magnesium-containing metal melt is arranged within the upper region of a retort together with the upper region of a crucible-like condensation vessel with a cover located above its opening, wherein the retort tapering in its lower region closely surrounds the lower part of the crucible-like condensation vessel, and in that the retort is connected via a barrier unit to a supply chamber, which is connected via a line and a valve to a vacuum pump, via a second line to a vacuum measuring instrument, and via a third line and a valve, selectively in series with a flow and/or pressure regulation apparatus, to an inert gas source, and in that at least part of the upper region of the retort can be heated by at least one heating element which is arranged externally around this region and can be controlled to constant temperature, whereas the lower region of the retort can be heated, either directly by at least one heating element which is arranged externally around this region and can be controlled to constant temperature and/or indirectly by insulation which is arranged around this region and protects against heat extraction, in order to attain a desired temperature profile.
5. The apparatus according to Claim 4, characterised in that the barrier unit at a temperature above the melting point is arranged between the upper end face of the

retort located below and below the lower end face of the supply chamber, and in that the supply chamber can be sealed outwardly by a selectively cooled flange arranged on the upper end face of said supply chamber, wherein the barrier unit can be actuated by a rod guided outwardly in a vacuum-tight manner through the flange and can be removed together with the flange following the end of the distillation process or of a furnace cycle once cooling has been performed, and in that the clear opening of the barrier unit is of such a size that new magnesium-containing material is introduced into the evaporation zone through this opening and the condensed and solidified pure magnesium can also be removed from the crucible-like condensation vessel following temporary removal of the cover arranged above its opening.

6. The apparatus according to Claim 4, selectively in combination with Claim 5, characterised in that the retort and the barrier unit consist of stainless steel or a heat-resistant steel or a superalloy.
7. The apparatus according to Claim 4, selectively in combination with Claim 5 and/or 6, characterised in that the crucible-like condensation vessel and the cover arranged above its opening consist of a high-purity graphite.
8. The apparatus according to Claim 4, and one of Claims 5–7, individually or in combination, characterised in that the crucible-like condensation vessel has an inner lateral surface opening conically upwards.
9. The apparatus according to Claim 4, and one of claims 5–8, individually or in combination, characterised in that the condensation vessel has, at least in its lower region, an upwardly opening conical outer lateral surface, which sits in a sealing manner on the correspondingly conically formed inner lateral surface of the lower region of the retort.
10. The apparatus according to Claim 4, and one of Claims 5–8, individually or in combination, characterised in that the condensation vessel, at least in its lower region, has a cylindrical or downwardly opening conical lateral surface, which sits in

a largely sealing manner on the correspondingly conically formed inner lateral surface of the lower region of the retort, and in that, on the lower end face of the retort, a flange provided selectively with an inert gas line is arranged, following the temporary removal of which the crucible-like condensation vessel can be removed downwardly from the retort between two furnace cycles and once cooling has been performed.

11. The apparatus according to Claim 4, and one of Claims 5–10, individually or in combination, characterised in that the crucible-like condensation vessel is arranged with its longitudinal axis along the longitudinal axis of the central symmetrical retort, wherein the part of the crucible-like condensation vessel present in the upper region of the condensation vessel is separated, by a partition wall surrounding it closely and connecting it tightly at the bottom to the retort, from the starting material surrounding it in a concentrated manner in the form of the magnesium-containing metal melt, wherein this partition wall preferably consists of the same material as the retort.