(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 469 091 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
20.10.2004 Bulletin 2004/43

(51) Int Cl.[7]: **C22C 1/02**

(21) Application number: **04007680.4**

(22) Date of filing: **30.03.2004**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LI LU MC NL PL PT RO SE SI SK TR
Designated Extension States:
AL LT LV MK

(30) Priority: **10.04.2003 JP 2003106922**

(71) Applicant: **Kabushiki Kaisha Toyota Chuo Kenkyusho**
Aichi-gun, Aichi-ken, 480-1192 (JP)

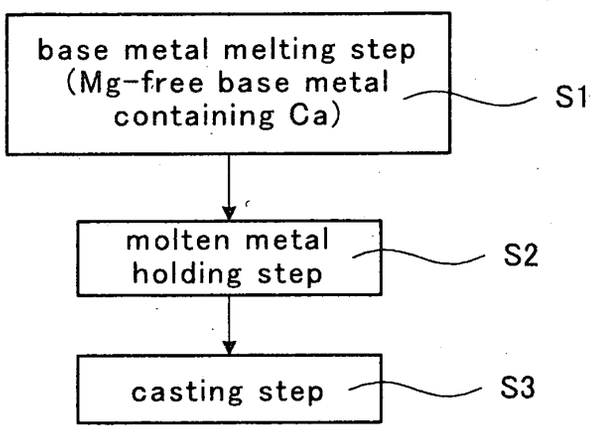
(72) Inventors:
- **Ikuno, Hajime, K.K. Toyoto Chuo Kenkyusho**
  Aichi-gun Aichi-ken 480-1192 (JP)
- **Hohjo, Hiroshi, K.K. Toyoto Chuo Kenkyusho**
  Aichi-gun Aichi-ken 480-1192 (JP)
- **Sugimoto, Yoshihiko,**
  K.K. Toyoto Chuo Kenkyusho
  Aichi-gun Aichi-ken 480-1192 (JP)
- **Ueda, Isamu, K.K. Toyoto Chuo Kenkyusho**
  Aichi-gun Aichi-ken 480-1192 (JP)
- **Iwahori, Hiroaki, K.K. Toyoto Chuo Kenkyusho**
  Aichi-gun Aichi-ken 480-1192 (JP)

(74) Representative: **Schmidtchen, Jürgen**
Kramer Barske Schmidtchen,
European Patent Attorneys
Patenta
Radeckestrasse 43
81245 München (DE)

(54) Method of producing Al alloy with low Ca content and base material for producing Al alloy with low Ca content

(57) To present a method of producing Al alloy with low Ca content capable of reducing Ca securely at low cost, and an Al alloy base metal applicable to such producingmethod. This is a method of producing Al alloy with low Ca content containing Ca by 0.002 mass % or less. The method comprises a base metal melting step S1 for melting an Al alloy base metal containing Ca by 0.003 mass % or more and containing Mg by 1 mass % or less, a molten metal holding step S2 for reducing the Ca content to 0.002 mass % or less by exposing the surface of molten metal obtained at the base metal melting step S1 to the atmosphere for 20 minutes or more, and a casting step S3 for casting the molten metal into a mold of desired shape. It is preferable that the Al alloy base metal contains Mg by 0.2 mass % or less. It is preferable that the method further comprises a Mg adding step for adding a desired amount of Mg to the molten metal posterior to the molten metal holding step.

FIG. 1



EP 1 469 091 A1

Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to a method capable of producing Al alloy with low Ca content at low cost, and an Al alloy base metal applicable in this producing method.

Discussion of the Background

[0002] In an Al alloy, Ca existing as impurities have various adverse effects on the alloy characteristics, and unnecessary Ca has been decreased as much as possible by various techniques. In Al alloy casting manufacturers, because an Al alloy base metal with low Ca content made of expensive metal Si with low Ca content and the like has been used, it has been difficult to lower the product cost.

[0003] In a conventional Ca reducing method, for example, patent document 1 discloses a "method of removing calcium from aluminum or its alloy." The method of removing calcium from aluminum or its alloy in patent document 1 is characterized by adding boron source for generating free boron inmoltenmetal of aluminum or its alloy, and removing the calcium contained in the molten metal of aluminum or its alloy as calcium-boron compound.

[0004] Moreover, patent document 2 discloses a "producing method of Al-Cu-Si-Mg system alloy" for making a ingot of Al-Cu-Si-Mg system alloy containing Cu by 0.5 to 5%, Si by 6 to 20%, Mg by 0.3 to 4% as essential element and Ni and/or Mn as arbitrary element, in which the molten metal containing at least one or more elements above reacts with aluminum potassium fluoride or aluminum potassium fluoride and aluminum fluoride, and thereby the Ca content in the molten metal is reduced.

[Patent document 1]
JP 1986-28005 (S61-28005) Examined Patent Application (Kokoku)
[Patent document 2]
JP 1986-51616 (S61-51616) Examined Patent Application (Kokoku)

[0005] However, in the method of the patent document 1, the Ca reducing effect is expected, but an additional process of "adding boron, letting stand, and removing slag" is needed, and the cost is increased. Therefore, the application scope of this Ca reducing method has been limited. Besides, the residual boron as inclusions may be mixed into the ingot, and its performance or workability may be impaired.

[0006] However, in the method of patent reference 2, the Ca reducing effect is expected also, but an additional process is needed, and the cost is increased.

SUMMARY OF THE INVENTION

[0007] The present invention has been made in consideration of such conventional problems, and an object of the present invention is to provide a method of producing Al alloy with low Ca content capable of reducing Ca securely at low cost, and an Al alloy base metal applicable to such producing method.

[0008] According to the first aspect of the present invention, a method of producing Al alloy with low Ca content containing Ca by 0.002 mass % or less, comprises:

a base metal melting step for melting an Al alloy base metal containing Ca by 0.003 mass % or more and Mg by 1 mass % or less, a molten metal holding step for reducing the Ca content to 0.002 mass % or less by exposing the surface of molten metal obtained at the base metal melting step to the atmosphere for 20 minutes or more, and a casting step for casting the molten metal into a mold of desired shape.

[0009] What should be noted in the method of producing Al alloy with low Ca content in the present invention is as follows: an Al alloy base metal of relatively high content of Ca by 0.003 mass % or more, and relatively low content of Mg by 1 mass % or less, are used, and the molten metal holding step is indispensable. Herein, the concept of Al alloy base metal includes not only raw material available as base metal, but also any material which can be melted, either one type or mixture of plural materials.

[0010] In the molten metal holding step, as described above, the surface of the molten metal is exposed to the atmosphere for 20 minutes or more. As a result, Ca contained in the molten metal is oxidized in preference on the molten metal surface, and an oxide layer containing Ca is formed, and by removing this surface layer on the molten metal after the molten metal holding step, Ca is removed from the molten metal. Therefore, owing to this molten metal holding process, the Ca content in the molten metal can be decreased sufficiently. Meanwhile, by exposing the molten metal to the atmosphere for more than 60 minutes, the Ca content can be effectively lowered, and further by exposing for more than 120 minutes, the effect can be further enhanced.

[0011] Since the Ca content can be lowered in the molten metal holding step following the base metal melting step, as the Al alloy base metal, an inexpensive base metal with a relatively high Ca content of 0.003 mass % or more can be used actively. As a result, because of lowing of the material cost, the obtained Al alloy with low Ca content is also inexpensive. On the other hand, when the Al alloy base metal with Ca content of less than 0.003 mass %, the cost of the base metal become expensive.

[0012] Further, the Mg content in the Al alloy base metal should be 1 mass % or less. Therefore, in the molten metal holding step, the Ca reducing effect can be obtained sufficiently in a practical holding time range. It is because Mg is oxidized in preference to Ca in the molten metal containing much Mg, Ca is hardly oxidized. Hence, if the Mg content in the Al alloy base metal is over 1 mass %, the Ca reducing effect in the molten metal holding step is lowered.

[0013] According to the second aspect of the present invention, a base metal for the method of producing Al alloy with low Ca content of the first aspect of the present invention,

characterized by that the Ca content is 0.003 mass % or more and the Mg content is 1 mass % or less.

[0014] The base metal for producing Al alloy with low Ca content of the present invention is an Al alloy base metal intended to be used in the method of producing the first aspect of the invention. This Al alloy base metal contains, as mentioned above, Ca by 0.003 mass % or more and Mg by 1 mass % or less. Therefore, the Al alloy base metal is inexpensive, and is high in Ca reducing effect in the subsequentmoltenmetal holding step. On the other hand, if the Ca content is less than 0.003 mass %, the price become higher, or if the Mg content exceeds 1 mass %, the Ca reducing effect in the subsequent molten metal holding step is lowered.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015]

Fig. 1 is an explanatory diagram of producing process of Al alloy with low Ca content in embodiment 1.
Fig. 2 is an explanatory diagram showing transition of Ca analytical values in embodiment 1.
Fig. 3 is an explanatory diagram of producing process of Al alloy with low Ca content in embodiment 2.
Fig. 4 is an explanatory diagram showing transition of Ca analytical values in embodiment 2.
Fig. 5 is an explanatory diagram of producing process of Al alloy with low Ca content in embodiment 3.
Fig. 6 is an explanatory diagram showing transition of Ca analytical values in embodiment 3.
Fig. 7 is an explanatory diagram showing transition of Ca analytical values in embodiment 4.
Fig. 8 is an explanatory diagram showing transition of Ca analytical values in embodiment 5.
Fig. 9 is an explanatory diagram showing transition of Ca analytical values in embodiment 6.
Fig. 10 is an explanatory diagram showing transition of Ca analytical values in embodiment 7.
Fig. 11 is an explanatory diagram showing transition of Ca analytical values in embodiment 8.
Fig. 12 is an explanatory diagram showing transition of Ca analytical values in embodiment 9.
Fig. 13 is an explanatory diagram showing transition of Ca analytical values in embodiment 10.
Fig. 14 is an explanatory diagram showing transition of Ca analytical values in embodiment 11.
Fig. 15 is an explanatory diagram showing transition of Ca analytical values in embodiment 12.
Fig. 16 is an explanatory diagram showing transition of Ca analytical values in embodiment 13.
Fig. 17 is an explanatory diagram showing transition of Ca analytical values in embodiment 14.
Fig. 18 is an explanatory diagram of producing process of Al alloy with low Ca content in embodiment 15.
Fig. 19 is an explanatory diagram showing transition of Ca analytical values in embodiment 15.
Fig. 20 is an explanatory diagram showing transition of Ca analytical values in embodiment 16.
Fig. 21 is an explanatory diagram showing transition of Ca analytical values in embodiment 17.
Fig. 22 is an explanatory diagram showing transition of Ca analytical values in embodiment 18.
Fig. 23 is an explanatory diagram showing transition of Ca analytical values in embodiment 19.
Fig. 24 is an explanatory diagram showing transition of Ca analytical values in embodiment 20.

DESCRIPTION OF REFERENCE NUMERALS

[0016]

S1 Base metal melting step
S15 Deoxidation step
S16 Deoxidation + degassing step
S2 Molten metal holding step
S25 Mg adding step
S3 Casting step

Description of the Preferred Embodiments

[0017] In the first aspect of the invention, it is preferable that the Al alloy base metal contains Mg by 0.2 mass % or less. In this case, the Ca reducing effect is further enhanced in the molten metal holding step. In addition, the content of Mg should be as low as possible, and its lower limit is preferred to be a level of inevitable impurity.

[0018] Moreover, it is preferable that the method further comprises a Mg adding step for adding a desired amount of Mg to the molten metal posterior to the molten metal holding step. In this case, the Al alloy of low Ca content containing Mg can be produced ef f iciently at low cost. That is, as mentioned above, as the Al alloy base metal, an inexpensive base metal of relatively high content of Ca is used, and the Ca content is reduced efficiently in the molten metal holding step. Subsequently, a desired amount of Mg is added. As a result, without lowering the Ca reducing effect in the molten metal holding step, the Al alloy with low Ca content having a desired'amount of Mg can be produced efficiently at low cost.

[0019] Moreover, it is preferable that the method further comprises a Ca adding step for adding a desired trace amount of Ca to the molten metal posterior to the molten metal holding step. In this case, the Al alloy of low Ca content containing a trace of Ca can be produced precisely at low cost. That is, as mentioned above, as the Al alloy base metal, an inexpensive base metal containing much higher level of Ca than the desired Ca amount is used, and the Ca content is once decreased more than the desired Ca amount by conducting the molten metal holding step. Subsequently, a trace of Ca is added to reach a desired amount. As a result, even if an inexpensive base metal is used, the Al alloy with low Ca content having a desired trace amount of Ca intentionally can be produced precisely at low cost.

[0020] Moreover, it is preferable that the method further comprises a deoxidation step for removing nonmetallic inclusions such as oxides in the molten metal prior to the molten metal holding step. In this case, the Ca content can be also decreased in the deoxidation step, and an excellent Ca removal effect is obtained by the synergistic effect with the molten metal holding step. Moreover, Ca removal effect is higher in the process sequence of deoxidation step followed by molten metal holding step as compared with the reverse sequence.

[0021] Deoxidation process is realized by various known methods. Usually, flux containing halogen compound is used. Forexample, flux powder is added to molten metal, stirred, and let stand for about 10 minutes, and slag is removed. By this deoxidation process, Ca reacts with flux to produce slag, and it is removed from the molten metal. As the flux for deoxidation, mainly Na system compound or K system compound are used, and both have almost the same Ca removal effects.

[0022] Moreover, it is preferable that the method further comprises a degassing step for removing hydrogen in the molten metal, between the deoxidation step and the molten metal holding step, or after the molten metal holding step. In this case, reducing effect of Ca content can be further improved. At the same time, porosity hardly occurs, and the alloy of low Ca can be obtained efficiently and relatively at low cost.

[0023] Practical methods of the degassing step include, for example, a vacuum degassing method of holding the molten metal in vacuum, and a gas bubbling method of blowing Ar or N_2 gas into the molten metal.

[0024] Moreover, it is preferable that the Al alloy base metal contains Si by 4 mass % or more. If the Al alloy base metal contains Si, Ca is often contained as impurities. In particular, when inexpensive Si raw material of low purity Si is used, the Ca content is high, and the method of the present invention is particularly effective, and practical effects are significant.

[0025] As the inexpensive Si raw material of low purity Si, metal Si of high Ca content containing Ca by 300 ppm or more is known. Al alloy base metal obtained by melting this metal Si of high Ca content together with other components and solidifying could include Ca by 0.003 mass % or more. Therefore, when this Al alloy base metal is used by melting (remelting), the producing method of the present invention is particularly effective.

[0026] Moreover, it is preferable that the desired Al alloy with low Ca content is an alloy containing Mg by 7 mass % or less, Si by 4 to 25 mass %, Cu by 7 mass % or less, Fe by 1.5 mass % or less, and Ni by 7 mass % or less. In this case, the obtained Al alloy with low Ca content is an alloy excellent in strength and heat resistance. In this case, too, a sufficient Ca reducing effect of the invention is obtained.

[0027] The reasons for setting the limit contents of the elements are briefly described below.

Mg: 7 mass % or less

[0028] If Mg content exceeds 7 mass %, compounds containing Mg are much crystallized, and ductility is extremely lowered.

Cu: 7 mass % or less

[0029] If Cu content exceeds 7 mass %, compounds containing Cu are much crystallized, and ductility is extremely lowered. Besides, porosity may increase, and fatigue characteristic may be lowered.

Si: 4 to 25 mass %

[0030] If Si content is less than 4%, flow of molten metal become poor and porosity is likely to occur. On the other hand, if Si content exceeds 25%, coarse primary crystal Si is much produced, and ductility and toughness at low temperature may be extremely lowered. Besides, machinability may be extremely lowered. Or melting temperature becomes extremely higher, and various problems such as oxidation of moltenmetal or increase of hydrogen content are caused.

[0031] To obtain a hypereutectic structure, Si content of at least 10 mass % or more is needed. For the ease of hypereutectic solidifying, and for refinement of primary crystal Si, it is preferred to add P.

Fe: 1.5 mass % or less

[0032] By containing Fe, Fe compounds are produced as crystals. By dispersion hardening of this crystals, high temperature yield stress is enhanced. In the case Fe exceeds 1.5 mass %, coarse Fe compounds are produced, and ductility and toughness may be lowered. Herein, Fe compound is a general name of compounds containing Fe.

Ni: 7 mass % or less

[0033] By containing Ni, compounds containing Ni are produced as crystals. By dispersion hardening of this crystals, high temperature yield stress is enhanced. In the case Ni exceeds 7 mass %, coarse compounds containing Ni are much produced, and ductility and toughness are lowered.

[0034] It is further preferred to contain Ti, Zr, and V by 0.05 to 0.5 mass % each. By containing these components, the heat resistance of the alloy is further enhanced. If the contents are less than 0.05 mass%, the effects are small, or if exceeding 0.5 mass %, coarse compounds are produced, and ductility and toughness may be lowered.

[0035] Moreover, it is preferable that the desired Al alloy with low Ca content is an alloy containing Si by 10 to 25 mass %, and having a hypereutectic structure including primary crystal Si. In this case, in particular, an alloy excellent in strength and heat resistance is obtained.

[0036] Moreover, if the Si content is less than 10 mass %, as mentioned above, it is hard to obtain hypereutectic structure. On the other hand, if exceeding 25 mass %, as mentioned above, coarse primary crystal Si is much produced, and various problems are caused, such as ductility and toughness at low temperature are lowered, machinability is also lowered, oxidation of molten metal and hydrogen content are increased.

[0037] In the base metal of the second aspect of the invention for producing Al alloy with low Ca content of the first aspect of the invention, it is preferable that the Mg content is 0.2 mass % or less.

[0038] It is preferable that, Si is further contained in the base metal by 4 mass % or more. In order to producing the base metal containing Si by 4 mass % or more, an inexpensive raw material of low purity Si, for example, metal Si with high Ca content containing Ca by 300 ppm or more can be used.

Embodiments

[0039] The method of producing Al alloy with low Ca content, and the base metal for the method as the embodiments of the present invention are specifically described below while referring to Fig. 1 to Fig. 24.

Embodiment 1

[0040] The embodiment was carried out, as shown in Fig. 1, by executing a base metal melting step S1 of melting Al alloy base metal (Mg-free base metal containing Ca) containing Ca by 0.003 mass % or more and Mg content of 1 mass % or less, and a molten metal holding step S2 for exposing the surface of the molten metal obtained in the base metal melting step S1 to the atmosphere. Moreover, it was followed by a casting step S3 for casting the molten metal into molds sequentially by varying the holding time at the molten metal holding step S2, and the relation of the holding time of the molten metal holding step and the Ca content was determined.

[0041] More specifically, the Al alloy base metal was prepared by melting pure Al for industrial use (99.8%) in a graphite crucible, and adjusting the Ca content to 100 ppm (0.01 mass %) by using Al-0.25 mass % Ca. In this embodiment, the melting process for this adjustment is evaluated as the base metal melting step S1, and the holding time immediately after the adjustment is the holding time of exposure to the atmosphere in the molten metal holding step S2.

[0042] In the embodiment, the casting step S3 for casting the molten metal into molds of 40 mm in diameter and 25 mm in height was executed right after adjustment, after 20 minutes of holding, and 60 minutes of holding individually, and the Ca content in the obtained cast alloy was analyzed. In the base metal melting step S1 and molten metal holding step S2, the molten metal temperature was controlled in a range of 750 deg. C +/- 20 deg. C. The Ca content was analyzed by fluorescent X-ray method using standard sample.

[0043] Analysis result of Ca content is shown in Fig. 2. In the diagram, the axis of abscissas denotes the Ca analysis timing, and the axis of ordinate represents the Ca analytical value (ppm) .

[0044] As shown in the diagram, as the holding time in the molten metal holding step S2 became longer, the Ca content decreased. That is, in the initial stage, the Ca content was already reduced from 100 ppm to 34 ppm, but by holding for 60 minutes, it was further reduced notably to about half of 18 ppm.

Embodiment 2

[0045] The embodiment was carried out, as shown in Fig. 3, by increasing the Ca content in the Al alloy base metal to 180 ppm (0.018 mass %) more than in embodiment 1, and executing a Mg adding step S25 of adding Mg intentionally after holding for 180 minutes, and the relation of the holding time of the molten metal holding step S2 and the Ca content was determined same as in embodiment 1.

[0046] Results are shown in Fig. 4. As shown in the diagram, the initial Ca content was high at 54 ppm, but reduceddramatically as the holding time continued, and dropped to about 24 ppm in 60 minutes, and 14 ppm in 180 minutes. Afterwards, Mg was added by about 1 mass %, and analysis samples were obtained immediately after and 30 minutes later. By addition of Mg, the Ca content was not changed, and the nearly same content was maintained after 30 minutes. The final Mg content was 0.94 mass %. As known from this result, it is clear that the Al alloy with low Ca content containing Mg can be easily obtained by adding Mg after removing Ca by using an alloy of low content of Mg.

Embodiment 3

[0047] The embodiment was carried out, as shown in Fig. 5, by executing a deoxidation step S15 before the molten metal holding step S2 in the producing process in embodiment 2. The other operation is the same as in embodiment 2. In deoxidation process of the present embodiment, a commercial flux for Al deoxidation mainly composed of Na system halogen compound was added in the molten metal, stirred and let stand for 10 minutes, and the slag was removed.

[0048] Transition of Ca content in this embodiment is shown in Fig. 6. As known from the diagram, the Ca content was 48 ppm before the deoxidation process, and dropped to 19 ppm by the deoxidation process, and further declined to 10 ppm or less in 60 minutes. After 120

minutes, Mg was added by about 1.5 mass %, and it was let stand for further 60 minutes. The final Mg amount was 1.4 mass %. By addition of Mg, the Ca content was not changed, and kept at low level. It is known from this result that the deoxidation process further enhances the Ca removal effect, and by using a raw material of low purity containing Ca by more than 100 ppm, an alloy with an extremely low Ca content of 10 ppm or less can be easily obtained.

Embodiment 4

[0049] This embodiment is similar to embodiment 3, except that a commercial flux for deoxidation mainly composed of K system halogen compound for hypereutectic Al-Si alloy was used in the deoxidation step S15. Only the Ca content before Mg adding step in embodiment 3 was analyzed. Results are shown in Fig. 7. In this case, too, the deoxidation process and holding step extremely encouraged the Ca removal effect, and it is known that the Ca removal effect is obtained regardless of the type of the flux.

Embodiment 5

[0050] The present embodiment is similar to the producing method (Fig. 1) of embodiment 1, except that Al-0.5 mass % Mg alloy was used as Al alloy base metal, and deoxidation step was not carried out. In this case, too, as shown in Fig. 8, the initial Ca content was 35 ppm or more, but dropped to 11 ppm after holding for 60 minutes, and a sufficient Ca removal effect was obtained in spite of slight content of Mg.

Embodiment 6

[0051] In the present embodiment, an alloy containing Mg was used as Al alloy base metal as well as in embodiment 5, but deoxidation step was carried out. For the flux of deoxidation process, a commercial product mainly composed of Na system halogen compound is used. In this case, too, as shown in Fig. 9, the deoxidation process and holding step extremely encouraged the Ca removal effect, and instead of the high initial Ca content of 47 ppm, an alloy of high purity of 8 ppm or less Ca was obtained after holding for 60 minutes or more.

Embodiment 7

[0052] The present embodiment is similar to the method (Fig. 1) of embodiment 1, except that Al alloy containing Si was used as Al alloy base metal, and deoxidation step was not carried out.

[0053] More specifically, after melting pure Al for industrial use (99.8%) in a graphite crucible, low purity metal Si with high content of Ca was added, and Al-13.8 mass % Si alloy was obtained in the base metal melting step S1 (Fig. 1). It was followed by the molten metal holding step S2, and further by the casting step S3, and changes of Ca content were studied by sampling. The melting temperature and holding temperature were both 750 deg. C +/- 20 deg. C.

[0054] As shown in Fig. 10, since the Si of extremely low purity was used, the initial Ca content was very high levels of 70 ppm, but Ca was removed progressively along with the holding time, and it extremely dropped to 44 ppm after holding for 210 minutes.

Embodiment 8

[0055] In this embodiment, Al-25 mass % Si alloy base metal (Ca content of 150 ppm), which was made by using low purity Si as in the embodiment 7, was used as the melting material. This Al 25-mass % Si alloy is added to pure Al for industrial use (99.8%) melted in a graphite crucible. And the obtained ingot of Al-13.8 mass % Si alloy is used as the Al alloy base metal. In this embodiment, as shown in Fig. 5, the base metal melting step S1 was followed by deoxidation step S15 by using flux mainly composed of K system halogen compound. Further, as shown in Fig. 5, the molten metal holding step S2 was followed by Mg adding step S25.

[0056] As shown in Fig. 11, by the deoxidation process and subsequent holding step, Ca dropped extremely to quite low level of 10 ppm or less in 60 minutes. After 120 minutes holding, Mg was added, and it was let stand for further 60 minutes, but by addition of Mg and subsequent holding time, the Ca content was not changed substantially, and kept at low level of 10 ppm or less. It is known from this result that the deoxidation step S15 and molten metal holding step S2 can lower the Ca content to 10 ppm or less, and an alloy of extremely high purity is obtained in spite of using the raw material of low purity metal Si of extremely high content of Ca. Also by Mg adding step S25 is conducted at the final process, an alloy containing Mg with low Ca content can be obtained easily. Since the low purity metal Si is inexpensive, the industrial merit is outstanding because an alloy of high purity can be obtained in such a simple process.

Embodiment 9

[0057] In embodiment 9, the deoxidation step using a commercial flux mainly composed of Na system halogen compound is executed up to before the Mg adding step S25 instead of executing the deoxidation step S15 (Fig. 5) of embodiment 8. As shown in Fig. 12, the same Ca removal effect as in embodiment 8 was obtained, and it is known that the Ca removal effect is obtained regardless of the type of the flux.

Embodiment 10

[0058] Similar to the method of embodiments 8 and 9, molten metal of Al-13.8 mass % Si alloy was prepared, and pure Mg for industrial use was added to, and

Al-13.8 mass % Si-0.7 mass % Mg alloy was made as the Al alloy base metal. In the deoxidation step, a commercial flux mainly composed of K system halogen compound was used. In this step, the Mg adding step was not executed.

[0059] As shown in Fig. 13, the initial Ca content was 45 ppm or more, but it was extremely reduced by deoxidation process and holding step, and dropped to 15 ppm in 60 minutes and 12 ppm in 120 minutes. However, as compared with the embodiments 8 and 9 not containing Mg in the Al alloy base metal, the Ca content after holding 60 minutes was slightly higher. That is, in order to achieve an extremely low Ca content of 10'ppm or less, it is preferred to use an alloy not containing Mg, and add Mg in the final step after Ca removal.

Embodiment 11

[0060] In this embodiment, alloy with Ca which was added Al-12. 5 Si-3 Cu-0.8 Mg-2.4 Ni-0.4 Fe-0.4 Mn-0.2 Ti-0.1 Zr-0.1 V (mass %) alloy was used as the Al alloy base metal, and Al-0.25 mass % Ca was added to add Ca, and the same method (Fig. 1) as in embodiment 1 was conducted. Deoxidation step and Mg adding step were not executed.

[0061] As shown in Fig. 14, Ca amount fluctuate up to 60 minutes of holding, and the Ca removal effect is not clear, but by holding for 120 minutes or more, the Ca amount reduce to 5 ppm or less.

Embodiment 12

[0062] In this embodiment, deoxidation step S15 was added using commercial flux of K system halogen compound before the molten metal holding step S2 in embodiment 11.

[0063] As shown in Fig. 15, by deoxidation process and subsequent holding step, Ca reduced, and dropped to 9 ppm or less in 120 minutes or more.

[0064] As known from the results of this embodiment and embodiment 11, if fortifying elements of practical alloy such as Cu, Ni, Fe, Mn, and others is added, similar Ca removal is realized. However, to remove Ca more securely, it is effective to execute deoxidation process in addition to molten metal holding step. In the cast material from this alloywas extremelyhigh in strength as compared with the alloy not containing fortifying elements such as Cu, Ni, Fe, Mn, and others.

Embodiment 13

[0065] In this embodiment, as the Al alloy base metal, Al-13 Si-3 Cu-2.3 Ni-0.4 Fe-0.4 Mn-0.2 Ti-0.1 Zr-1.0 V (mass %) alloy was used, and the same method (Fig. 1) as in embodiment 1 was conducted. Deoxidation step and Mg adding step were not executed.

[0066] As shown in Fig. 16, Ca was removed credibly as the holding time progressed, and dropped to 8 ppm or less in 210 minutes. As known from the results, in the alloy system containing fortifying elements of practical alloy such as Cu, Ni, Fe, Mn, and others, stable Ca removal effect can be obtained more easily in an alloy not containing Mg.

Embodiment 14

[0067] In this embodiment, deoxidation step S15 was added using commercial flux of K system halogen compound before the molten metal holding step S2 in embodiment 13.

[0068] As shown in Fig. 17, Ca reduced by deoxidation process, and it dropped to 8 ppm or less after holding for 60 minutes. As known from this results, in the alloy system containing fortifying elements of practical alloy such as Cu, Ni, Fe, Mn, and others, a greater Ca removal effect is obtained in an alloy not containing Mg, and by the additional step of deoxidation, a high purity alloy with Ca content of 10 ppm or less can be obtained securely in a shorter time of holding.

Embodiment 15

[0069] In this embodiment, as the Al alloy base metal, Al-13 Si-3 Cu-2.3 Ni-0.4 Fe-0.4 Mn-0.2 Ti-0.1 Zr-0.1 V (mass %) alloy adjusted the initial Ca content to 20 ppm, was used. In this embodiment, as shown in Fig. 18, the base metal melting step S1 was followed by deoxidation + degassing step S16, that is, deoxidation process by using K system halogen compound flux, and degassing process of holding in a vacuum of 0.2 Torr or less for 40 minutes.

[0070] As shown in Fig. 19, by deoxidation and degassing process, the Ca amount dropped to 8 ppm or less, and low levels were maintained thereafter.

Embodiment 16

[0071] In this embodiment, Al-13.5 Si-3 Cu-2.3 Ni-0.4 Fe-0.4 Mn-0.2 Ti-0.1 Zr-0.1 V (mass %) alloy produced by adding molten metal of Al-25 mass % Si alloy (Ca content 150 ppm) which was made using the same low purity metal Si as in embodiments 8 and 9 to the Al alloy molten metal melted in a graphite crucible is used as the Al alloy base metal. In this embodiment, too, as shown in Fig. 18, the deoxidation + degassing step S16 was executed same as in embodiment 15.

[0072] As shown in Fig. 20, the initial Ca content in the base metal melting step S1 is estimated to be same as in embodiments 8 and 9, but after deoxidation and degassing process, it dropped extremely to 12 ppm, and after holding for 120 minutes, very low levels of 3 ppm or less were maintained.

[0073] As known from the results of this embodiment and embodiment 15, if the degassing process is conducted, similar Ca removal effect is obtained too, and even if metal Si of low purity is used as Si raw material,

by the execution of remelting, deoxidation, and molten metal holding steps, a practical alloy of high purity of extremely low Ca level can be obtained easily.

Embodiment 17

[0074] In this embodiment, Al-14 Si-3.2 Cu-2.6 Ni-0.4 Fe-0.4 Mn (mass %) alloy was used as the Al alloy base metal, and the base metal melting step S1 was executed (see Fig. 5) by melting in a graphite crucible. It was followed by deoxidation process using commercially available K system halogen compound flux, and changes of Ca amount in subsequent molten metal holding step were studied. In this embodiment, the Mg adding step S25 was not executed.

[0075] In this embodiment, when making the Al alloy base metal, the same low purity metal Si as in embodiments 8, 9, and 16 was used, and the Al alloy base metal was cast after deoxidation process. As the base metal melting step S1, remelting of the above Al alloy base metal was executed.

[0076] As shown in Fig. 21, the Ca content in the initial phase of melting was 21 ppm. By the deoxidation step S15 after the base metal melting step S1, the Ca amount extremely dropped to 5 ppm or less, and very low level was maintained thereafter.

[0077] Thus, even if using metal Si of low purity as Si rawmaterial, by execution of deoxidation and remelting (base metal melting step S1) when producing primary base metal, and the deoxidation step S15 andmolten-metal holding step S2 at the time of remelting, a practical alloy of high purity with very low Ca content can be obtained easily and stably.

[0078] In ordinary cast parts manufacture, the Al alloy base metal produced by the base metal manufacturer is cast after remelting, as the base metal melting step S1. So that, by setting the Mg amount low in the base metal obtained from the base metal manufacturer, adding Mg in the Mg adding step S25 after sufficiently removing Ca in the final process of casting parts, cast parts with high purity can be easily produced in the ordinary producing process.

[0079] In addition, by adding Mg after the final process, that is, after the molten metal holding step S2, cast parts of low Ca level containing Mg can be easily produced.

[0080] Besides, since it is easy to add Ca to adjust the Ca amount, if a trace of Ca is desired for improving the material structure, the Ca amount can be adjusted similarly after the final process, that is, after the molten metal holding step S2. In the alloy containing Mg, since gas absorption (to contain hydrogen) is likely to occur in the base metal melting step S1 and molten metal holding step S2, by processing up to the final process in the state of alloy free of Mg, adding Mg before the casting step 3, so that cast parts of high quality practically free from casting defects can be easily obtained.

Embodiment 18

[0081] This embodiment is a example of assuming the Al alloy base metal with Mg content of 0.1 mass % was used by adding pure Mg in the base metal melting step S1 of embodiment 17 to adjust the Mg content to 0.1 mass %. The other operation is same as in embodiment 17.

[0082] As shown in Fig. 22, if Mg is contained by 0.1 mass %, a notable Ca removal effect is obtained same as in the case not containing Mg.

Embodiment 19

[0083] This embodiment is similar to embodiment 18, except that Mg was contained by 0.2 mass %. As shown in Fig. 23, a notable Ca removal effect is observed as in embodiment 18.

Embodiment 20

[0084] This embodiment is similar to embodiment 18, except that Mg was contained by 5 mass %. As shown in Fig. 24, a Ca removal effect was observed after the deoxidation step S15 and subsequent molten metal holding step S2, but as compared with the results of embodiments 17 to 19 with Mg amount of 0.2 mass % or less, or embodiment 6 with Mg amount of 0.8 mass %, the effect was moderate. Therefore, to obtain a favorable Ca removal effect, it is preferred to process an alloy of which Mg content is 1 mass % or less, and to obtain an optimum Ca removal effect, it is desired to process an alloy of which Mg content is 0.2 mass % or less. If desired to contain Mg, it may be added in the Mg adding step S25 after the Ca removal process, and hence an alloy containing Mg with low Ca content can be easily produced. If it is desired to add a trace of Ca for the purpose of improvement of the material structure, after Ca removal process, a necessary amount of Ca can be added in the Ca adding step after the molten metal holding step S2, so that an alloy containing a trace of Ca can be easily produced. It is explicitly stated that all features disclosed in the description and/or the claims are intended to be disclosed separately and independently from each other for the purpose of original disclosure as well as for the purpose of restricting the claimed invention independent of the compositions of the features in the embodiments and/or the claims. It is explicitly stated that all value ranges or indications of groups of entities disclose every possible intermediate value or intermediate entity for the purpose of original disclosure as well as for the purpose of restricting the claimed invention.

Claims

1. A method of producing Al alloy with low Ca content containing Ca by 0.002 mass % or less, comprising:

a base metal melting step for melting an Al alloy base metal containing Ca by 0.003 mass % or more and Mg by 1 mass % or less,
a molten metal holding step for reducing the Ca content to 0.002 mass % or less by exposing the surface of molten metal obtained at the base metal melting step to the atmosphere for 20 minutes or more, and
a casting step for casting the molten metal into a mold of desired shape.

2. The method of producing Al alloy with low Ca content as claimed in claim 1, wherein the Al alloy base metal contains Mg by 0.2 mass % or less.

3. The method of producing Al alloy with low Ca content as claimed in claim 1 or 2, further comprising a Mg adding step for adding a desired amount of Mg to the molten metal posterior to the molten metal holding step.

4. The method of producing Al alloy with low Ca content as claimed in any one of claims 1 to 3, further comprising a Ca adding step for adding a desired trace amount of Ca to the molten metal posterior to the molten metal holding step.

5. The method of producing Al alloy with low Ca content as claimed in any one of claims 1 to 4, further comprising a deoxidation step for removing nonmetallic inclusions such as oxides in the molten metal prior to the molten metal holding step.

6. The method of producing Al alloy with low Ca content as claimed in claim 5, further comprising a degassing step for removing hydrogen in the molten metal, between the deoxidation step and the molten metal holding step, or after the molten metal holding step.

7. The method of producing Al alloy with low Ca content as claimed in any one of claims 1 to 6, wherein the Al alloy base metal contains Si by 4 mass % or more.

8. The method of producing Al alloy with low Ca content as claimed in claim 7, wherein the desired Al alloy with low Ca content is an alloy containing Mg by 7 mass % or less, Si by 4 to 25 mass %, Cu by 7 mass % or less, Fe by 1.5 mass % or less, and Ni by 7 mass % or less.

9. The method of producing Al alloy with low Ca content as claimed in claim 8, wherein the desired Al alloy with low Ca content is an alloy containing Si by 10 to 25 mass %, and having a hypereutectic structure including primary crystal Si.

10. A base metal for the method of producing Al alloy with low Ca content of any one of claims 1 to 9,
characterized by that the Ca content is 0.003 mass % or more and the Mg content is 1 mass % or less.

11. The base metal as claimed in claim 10, wherein the Mg content is 0.2 mass % or less.

12. The base metal as claimed in claim 11, wherein Si is further contained by 4 mass % or more.

FIG. 1

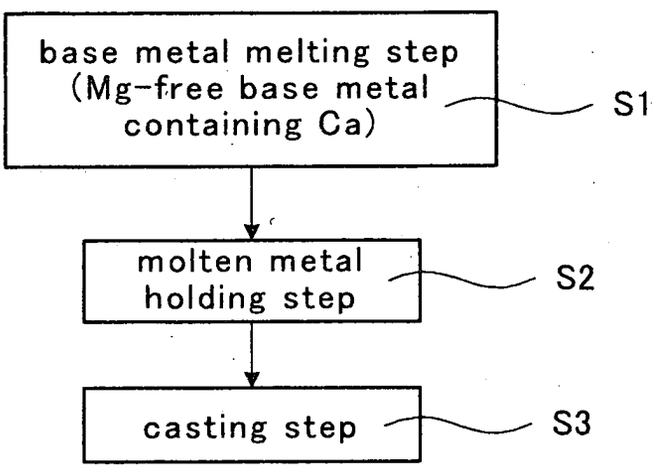

base metal melting step
(Mg-free base metal
containing Ca)
S1
molten metal
holding step
S2
casting step
S3

FIG. 2

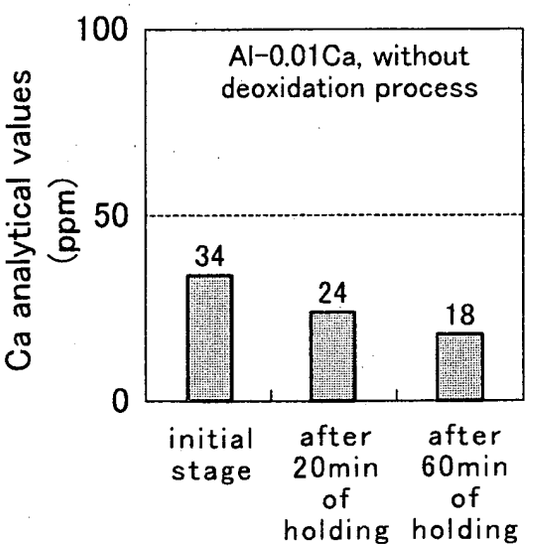

Al-0.01Ca, without deoxidation process
Ca analytical values (ppm)
100
50
0
34
24
18
initial stage
after 20min of holding
after 60min of holding

FIG. 3

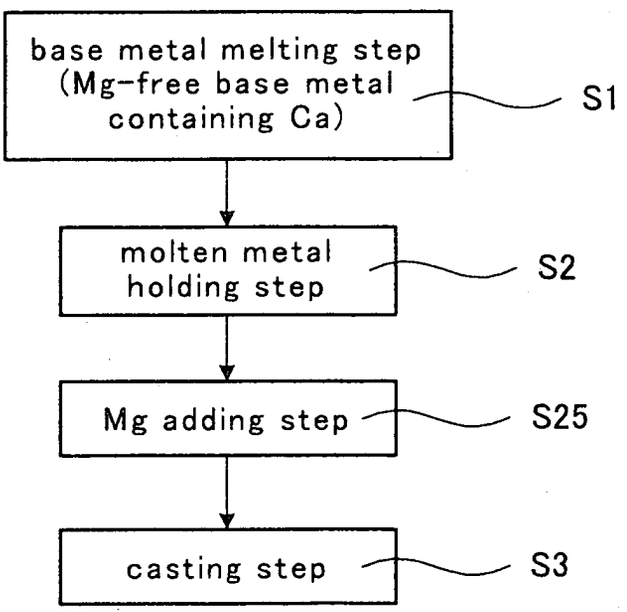

base metal melting step
(Mg-free base metal
containing Ca)
S1
molten metal
holding step
S2
Mg adding step
S25
casting step
S3

FIG. 4

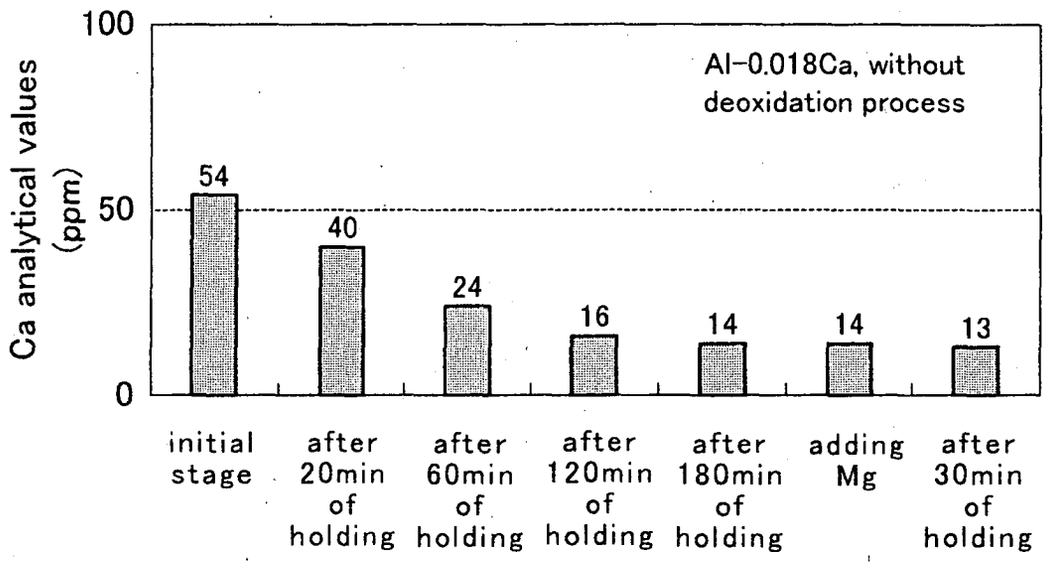

Ca analytical values (ppm)
100
50
0
Al-0.018Ca, without deoxidation process
54
40
24
16
14
14
13
initial stage
after 20min of holding
after 60min of holding
after 120min of holding
after 180min of holding
adding Mg
after 30min of holding

FIG. 5

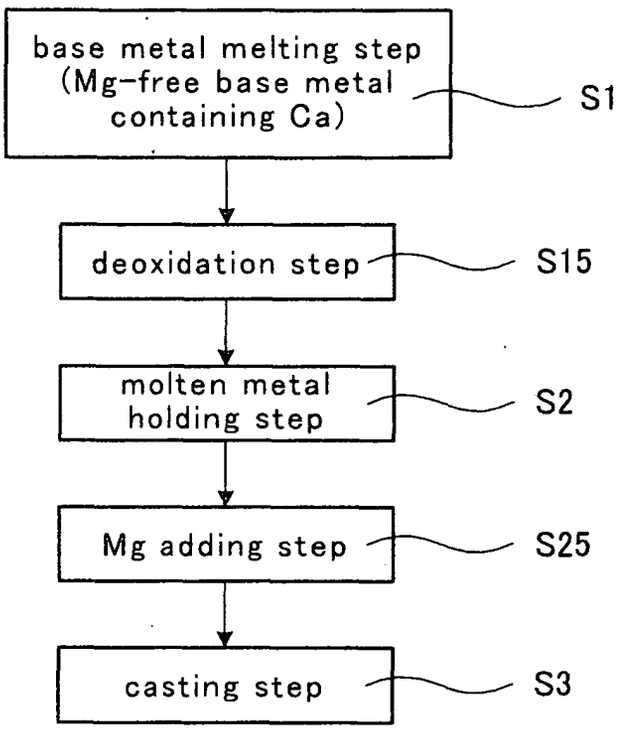

base metal melting step (Mg-free base metal containing Ca)
S1
deoxidation step
S15
molten metal holding step
S2
Mg adding step
S25
casting step
S3

FIG. 6

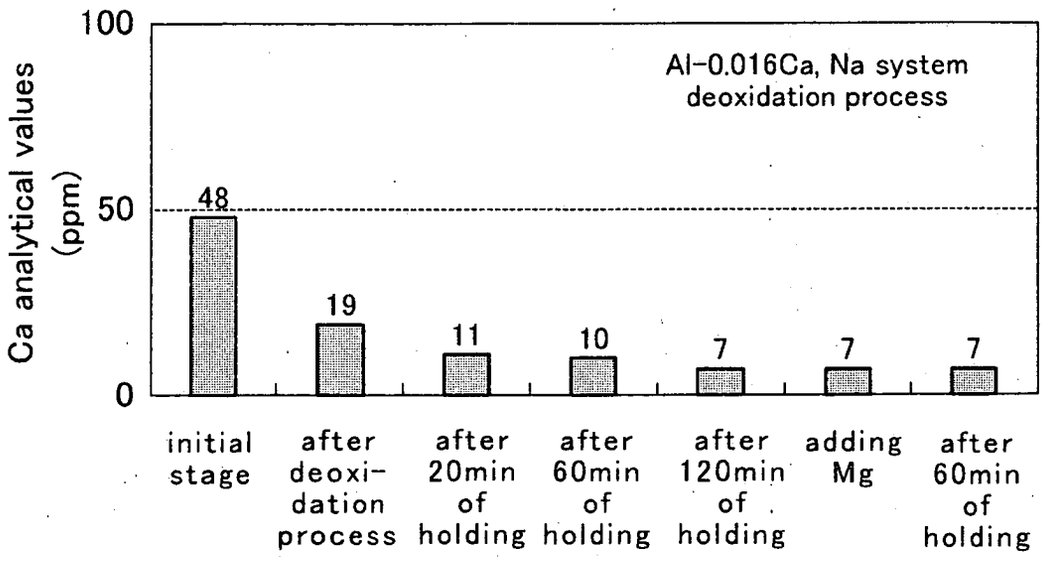

Ca analytical values (ppm)
100
50
0
Al-0.016Ca, Na system deoxidation process
48
19
11
10
7
7
7
initial stage
after deoxi-dation process
after 20min of holding
after 60min of holding
after 120min of holding
adding Mg
after 60min of holding

FIG. 7

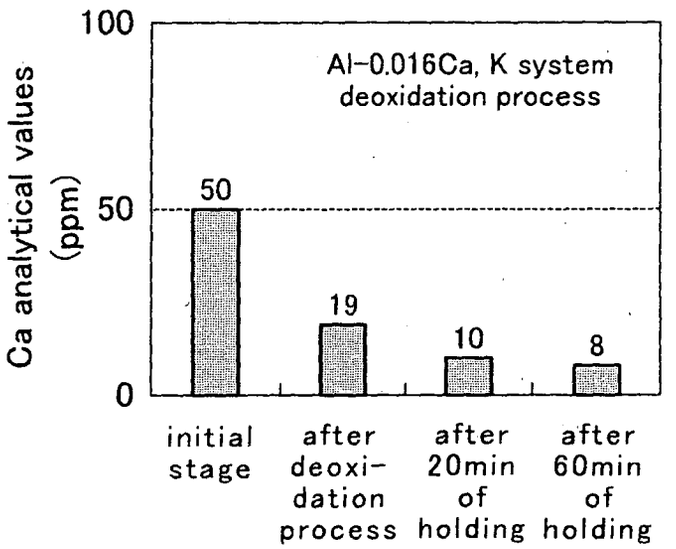

Ca analytical values (ppm)
100
50
0
Al-0.016Ca, K system deoxidation process
50
19
10
8
initial stage
after deoxi-dation process
after 20min of holding
after 60min of holding

FIG. 8

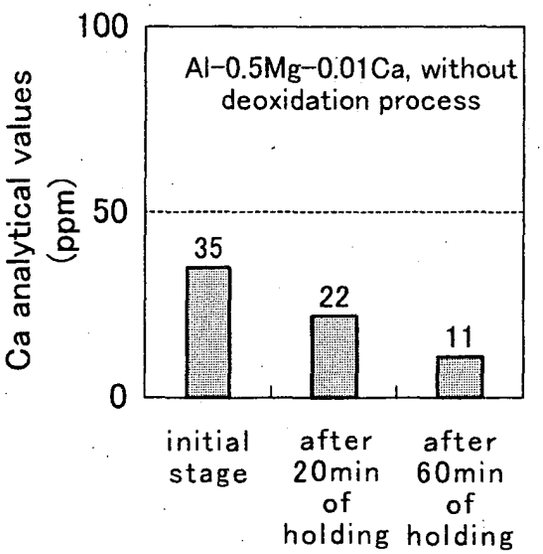

100
50
0
Ca analytical values (ppm)
Al-0.5Mg-0.01Ca, without deoxidation process
35
22
11
initial stage
after 20min of holding
after 60min of holding

FIG. 9

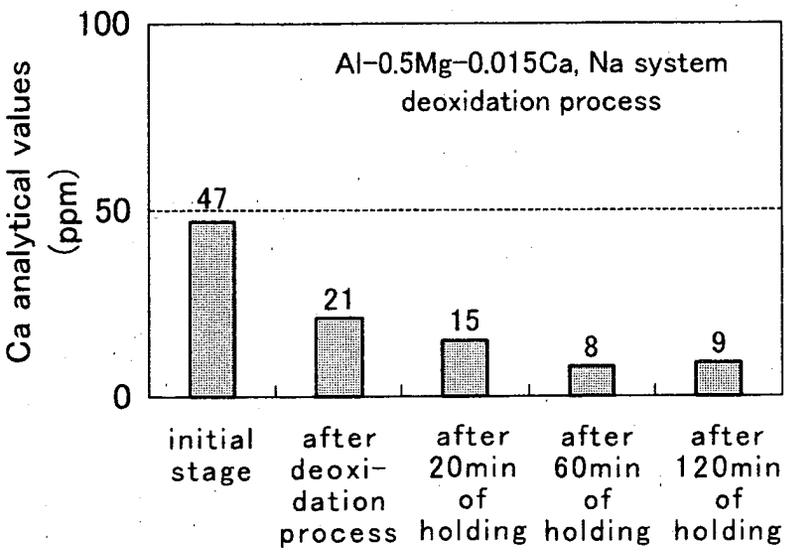

Al-0.5Mg-0.015Ca, Na system
deoxidation process
Ca analytical values (ppm)
100
50
0
47
21
15
8
9
initial stage
after deoxi-dation process
after 20min of holding
after 60min of holding
after 120min of holding

FIG. 10

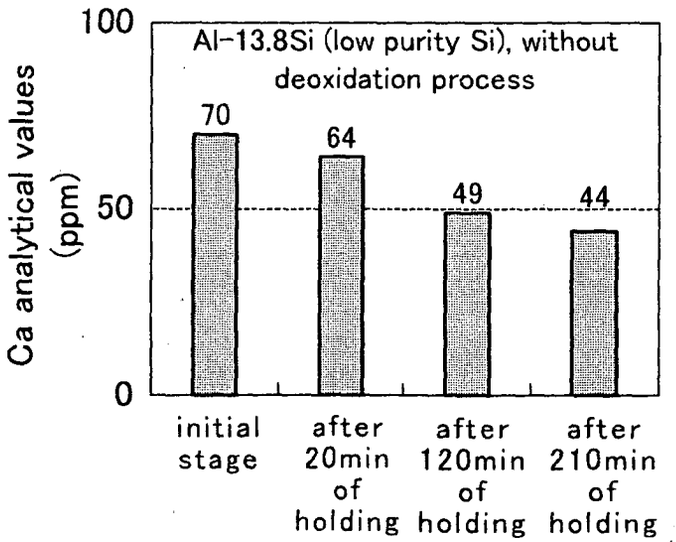

Al-13.8Si (low purity Si), without deoxidation process
Ca analytical values (ppm)
100
50
0
70
64
49
44
initial stage
after 20min of holding
after 120min of holding
after 210min of holding

FIG. 11

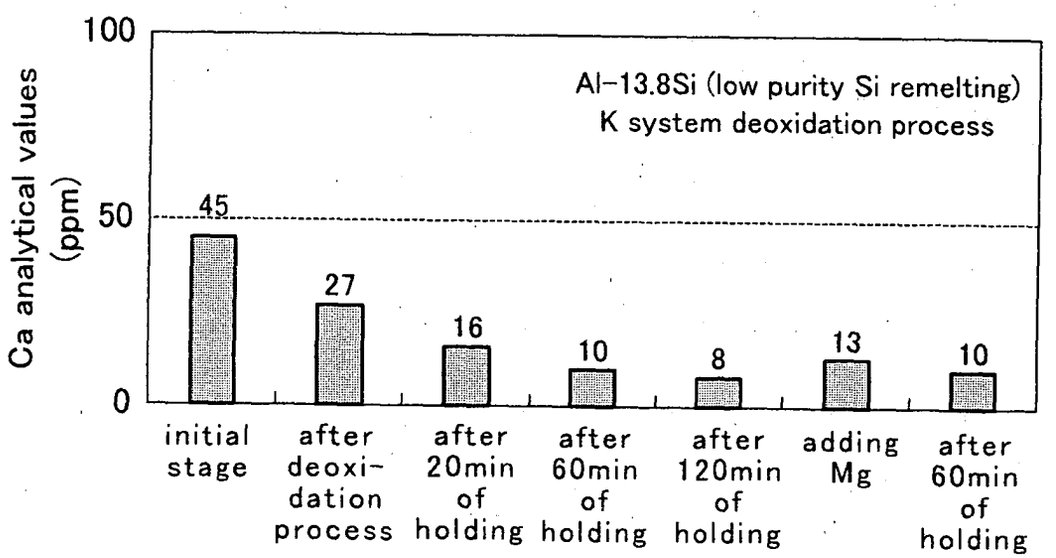

Ca analytical values (ppm)
100
50
0
Al-13.8Si (low purity Si remelting)
K system deoxidation process
45
27
16
10
8
13
10
initial stage
after deoxi-dation process
after 20min of holding
after 60min of holding
after 120min of holding
adding Mg
after 60min of holding

FIG. 12

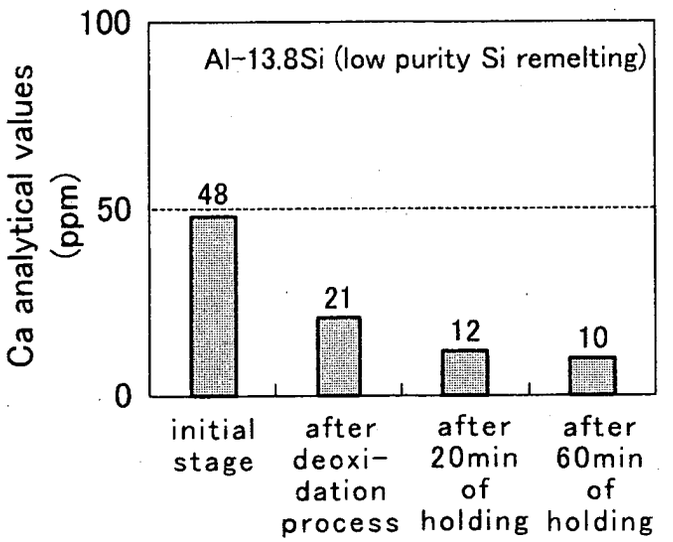

Al-13.8Si (low purity Si remelting)
Ca analytical values (ppm)
100
50
0
48
21
12
10
initial stage
after deoxi-dation process
after 20min of holding
after 60min of holding

FIG. 13

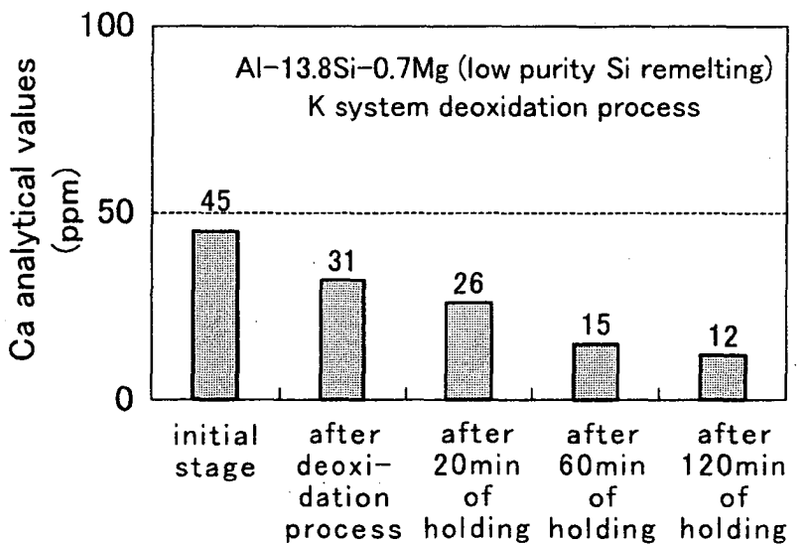

Al-13.8Si-0.7Mg (low purity Si remelting)
K system deoxidation process
Ca analytical values (ppm)
100
50
0
45
31
26
15
12
initial stage
after deoxi-dation process
after 20min of holding
after 60min of holding
after 120min of holding

FIG. 14

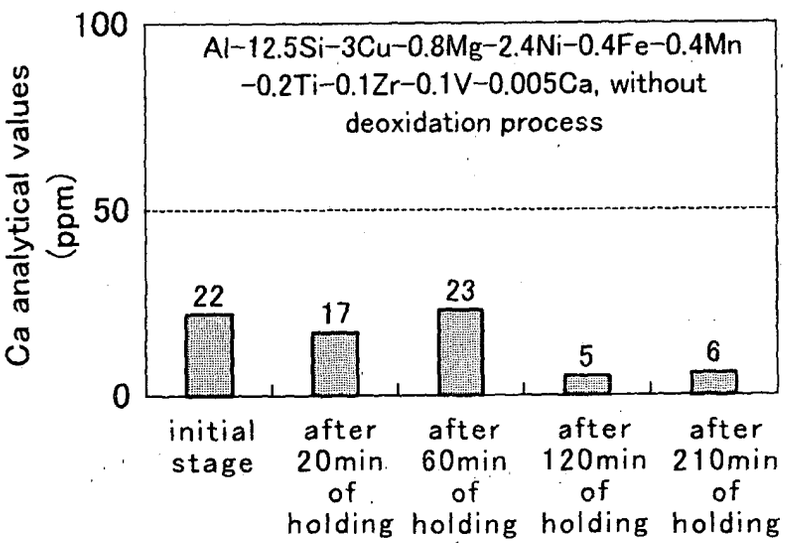

Al-12.5Si-3Cu-0.8Mg-2.4Ni-0.4Fe-0.4Mn
-0.2Ti-0.1Zr-0.1V-0.005Ca, without
deoxidation process
Ca analytical values (ppm)
100
50
0
22
17
23
5
6
initial stage
after 20min of holding
after 60min of holding
after 120min of holding
after 210min of holding

FIG. 15

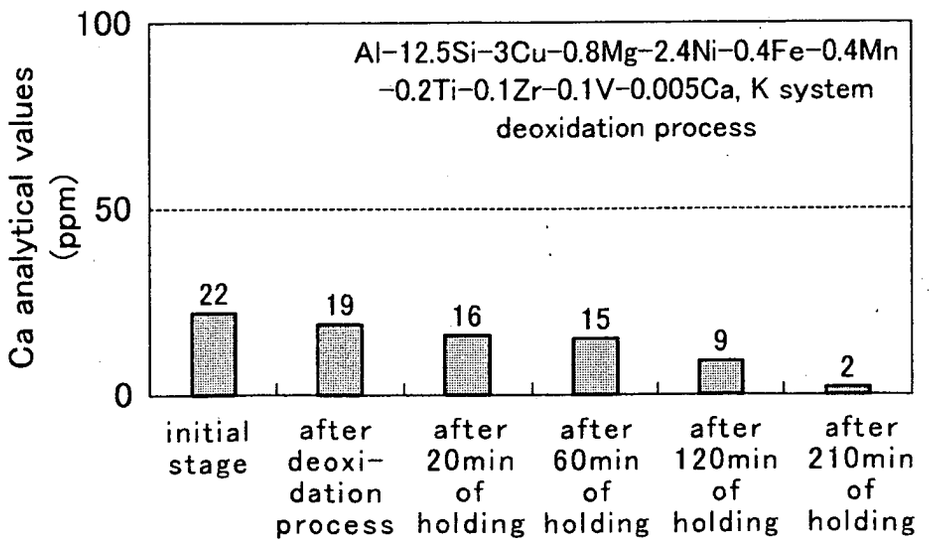

Al-12.5Si-3Cu-0.8Mg-2.4Ni-0.4Fe-0.4Mn
-0.2Ti-0.1Zr-0.1V-0.005Ca, K system
deoxidation process
Ca analytical values (ppm)
100
50
0
22
19
16
15
9
2
initial stage
after deoxi-dation process
after 20min of holding
after 60min of holding
after 120min of holding
after 210min of holding

FIG. 16

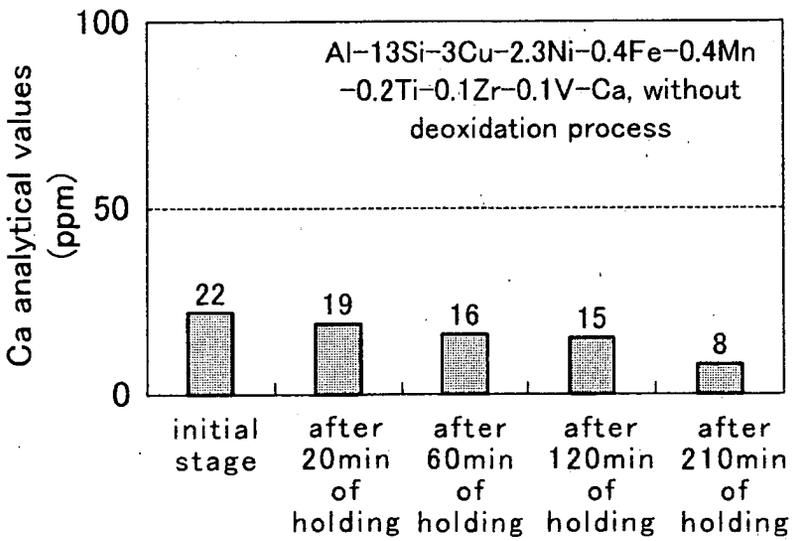

Ca analytical values (ppm)
100
50
0
Al-13Si-3Cu-2.3Ni-0.4Fe-0.4Mn -0.2Ti-0.1Zr-0.1V-Ca, without deoxidation process
22
19
16
15
8
initial stage
after 20min of holding
after 60min of holding
after 120min of holding
after 210min of holding

FIG. 17

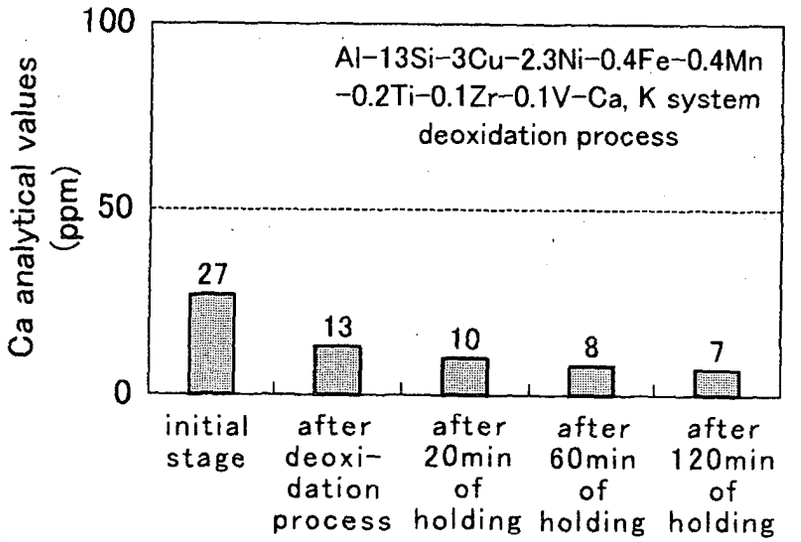

100
50
0
Ca analytical values (ppm)
Al-13Si-3Cu-2.3Ni-0.4Fe-0.4Mn -0.2Ti-0.1Zr-0.1V-Ca, K system deoxidation process
27
13
10
8
7
initial stage
after deoxi-dation process
after 20min of holding
after 60min of holding
after 120min of holding

FIG. 18

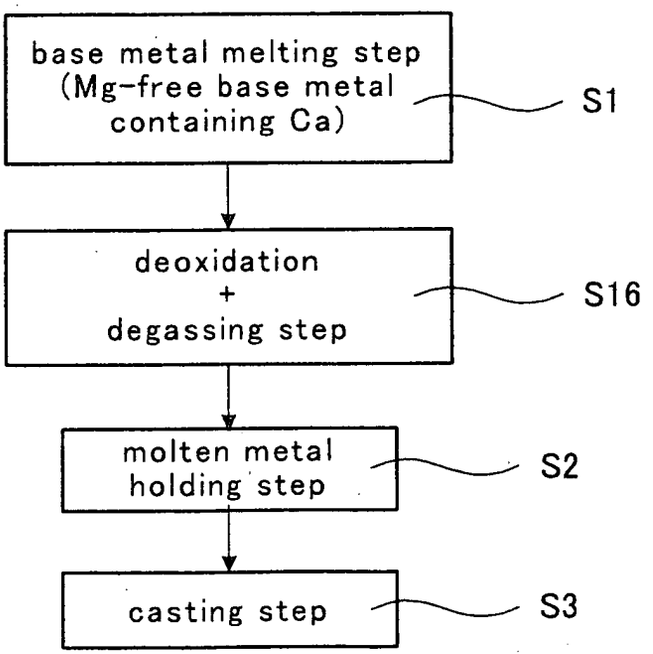

base metal melting step
(Mg-free base metal
containing Ca)
S1
deoxidation
+
degassing step
S16
molten metal
holding step
S2
casting step
S3

FIG. 19

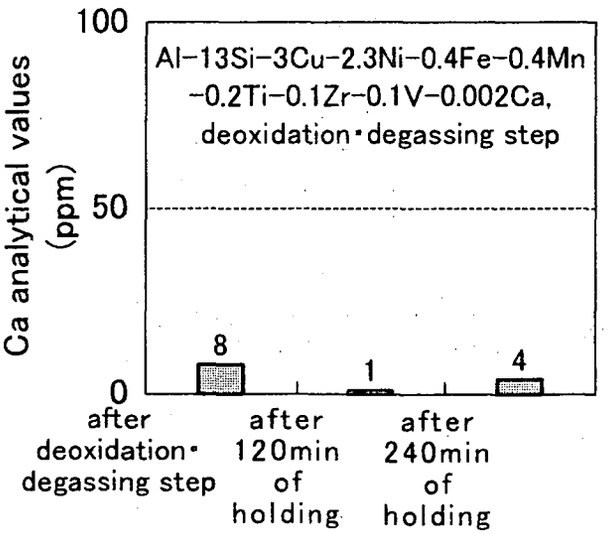

100
50
0
Ca analytical values (ppm)
Al-13Si-3Cu-2.3Ni-0.4Fe-0.4Mn -0.2Ti-0.1Zr-0.1V-0.002Ca, deoxidation·degassing step
8
1
4
after deoxidation· degassing step
after 120min of holding
after 240min of holding

FIG. 20

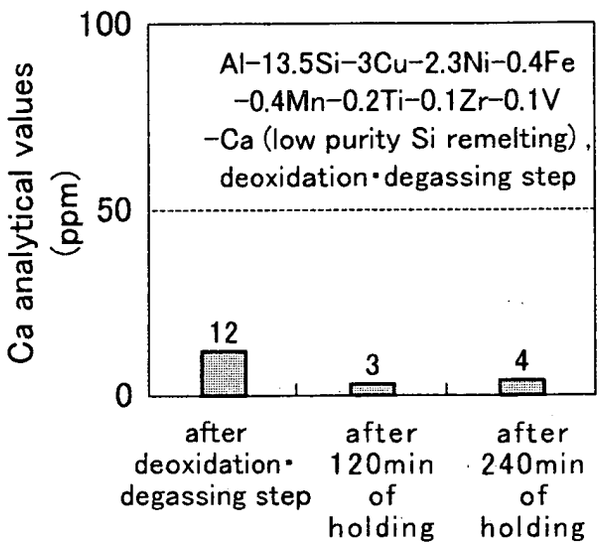

100
50
0
Ca analytical values (ppm)
Al-13.5Si-3Cu-2.3Ni-0.4Fe
-0.4Mn-0.2Ti-0.1Zr-0.1V
-Ca (low purity Si remelting),
deoxidation•degassing step
12
3
4
after deoxidation• degassing step
after 120min of holding
after 240min of holding

FIG. 21

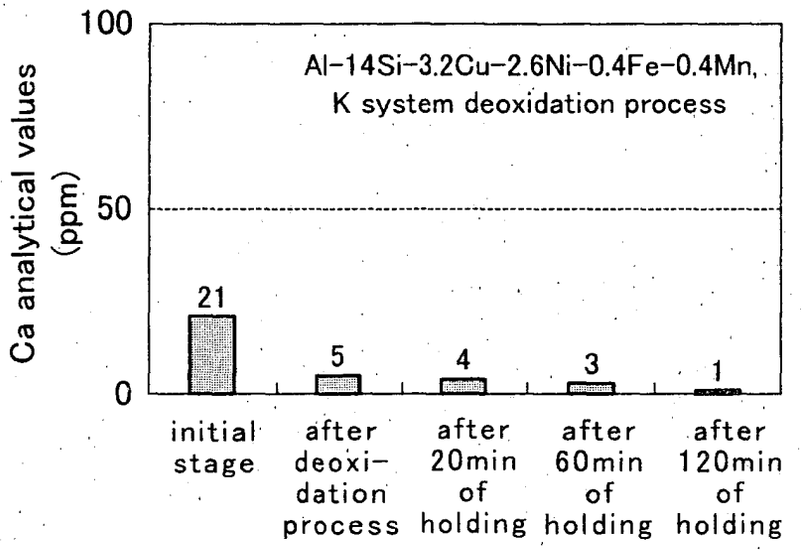

100
50
0
Ca analytical values (ppm)
Al-14Si-3.2Cu-2.6Ni-0.4Fe-0.4Mn,
K system deoxidation process
21
5
4
3
1
initial stage
after deoxi-dation process
after 20min of holding
after 60min of holding
after 120min of holding

FIG. 22

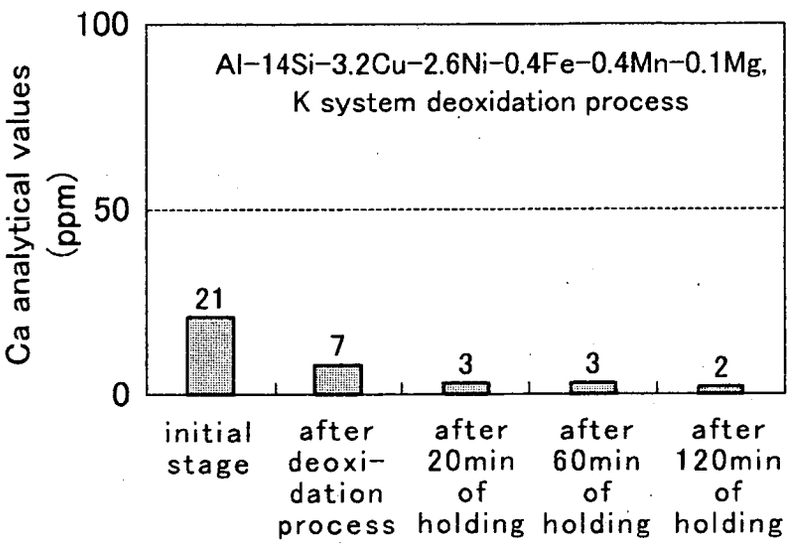

Al-14Si-3.2Cu-2.6Ni-0.4Fe-0.4Mn-0.1Mg,
K system deoxidation process
Ca analytical values (ppm)
100
50
0
21
7
3
3
2
initial stage
after deoxi-dation process
after 20min of holding
after 60min of holding
after 120min of holding

FIG. 23

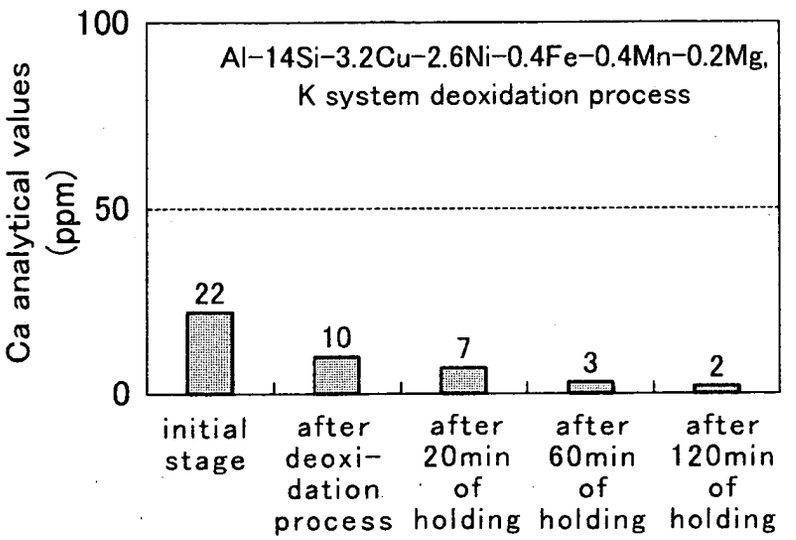
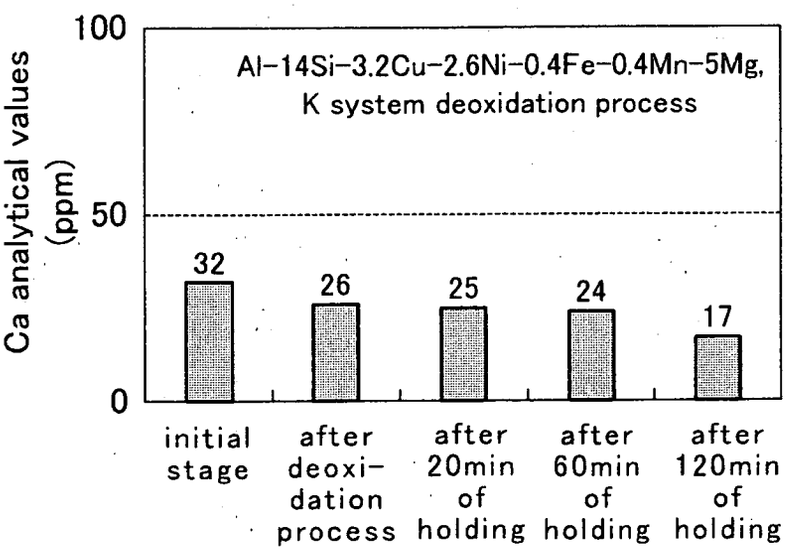

Al-14Si-3.2Cu-2.6Ni-0.4Fe-0.4Mn-0.2Mg,
K system deoxidation process
Ca analytical values (ppm)
100
50
0
22
10
7
3
2
initial stage
after deoxi-dation process
after 20min of holding
after 60min of holding
after 120min of holding

FIG. 24


Al-14Si-3.2Cu-2.6Ni-0.4Fe-0.4Mn-5Mg,
K system deoxidation process
Ca analytical values (ppm)
100
50
0
32
26
25
24
17
initial stage
after deoxi-dation process
after 20min of holding
after 60min of holding
after 120min of holding

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 04 00 7680

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.7)
X	US 4 099 965 A (BEGUIN JEAN CLAUDE ET AL) 11 July 1978 (1978-07-11) * the whole document * ---	1-12	C22C1/02
X,D	PATENT ABSTRACTS OF JAPAN vol. 005, no. 136 (C-069), 28 August 1981 (1981-08-28) -& JP 56 072143 A (SHOWA ALUM IND KK; OTHERS: 01), 16 June 1981 (1981-06-16) * the whole document * ---	1-12	
X	PATENT ABSTRACTS OF JAPAN vol. 017, no. 516 (C-1112), 17 September 1993 (1993-09-17) -& JP 05 140669 A (KOBE STEEL LTD), 8 June 1993 (1993-06-08) * the whole document * ---	10-12	
A	DE 199 18 766 A (ARNDT SCHAEFER CHEMIE UND UMWE) 2 November 2000 (2000-11-02) * the whole document * ---	1-12	
A	US 4 277 280 A (MONTGRAIN LUC) 7 July 1981 (1981-07-07) * the whole document * ---	1-12	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C22C
A	US 4 832 740 A (MEIER ERNST) 23 May 1989 (1989-05-23) * the whole document * -----	1-12	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	24 May 2004	Swiatek, R

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

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 04 00 7680

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

24-05-2004

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4099965 A	11-07-1978	FR 2325727 A1	22-04-1977
		BE 846538 A1	24-03-1977
		BR 7606277 A	07-06-1977
		CH 596320 A5	15-03-1978
		CS 199282 B2	31-07-1980
		DD 126556 A5	27-07-1977
		DE 2643075 A1	07-04-1977
		EG 12523 A	31-03-1979
		ES 451781 A1	16-08-1977
		GB 1546619 A	23-05-1979
		HU 175417 B	28-07-1980
		IT 1070554 B	29-03-1985
		JP 52046315 A	13-04-1977
		NL 7610664 A	29-03-1977
		NO 763220 A	29-03-1977
		RO 69749 A1	09-09-1982
		SE 7610365 A	27-03-1977
JP 56072143 A	16-06-1981	JP 1362128 C	09-02-1987
		JP 61028005 B	28-06-1986
JP 05140669 A	08-06-1993	JP 2989060 B2	13-12-1999
DE 19918766 A	02-11-2000	DE 19918766 A1	02-11-2000
		AU 4294400 A	10-11-2000
		CZ 20014114 A3	12-02-2003
		WO 0065110 A1	02-11-2000
US 4277280 A	07-07-1981	AU 531517 B2	25-08-1983
		AU 5015779 A	28-02-1980
		CA 1127852 A1	20-07-1982
		CH 645133 A5	14-09-1984
		DE 2934144 A1	06-03-1980
		DE 7924039 U1	14-02-1980
		ES 483576 A1	01-09-1980
		FR 2434211 A1	21-03-1980
		GB 2030597 A ,B	10-04-1980
		JP 1455513 C	25-08-1988
		JP 55031196 A	05-03-1980
		JP 63000497 B	07-01-1988
		NO 792725 A ,B,	26-02-1980
US 4832740 A	23-05-1989	AT 73171 T	15-03-1992
		DE 3868660 D1	09-04-1992
		EP 0285566 A1	05-10-1988
		NO 881370 A ,B,	03-10-1988

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82