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(71) Applicant: **Kabushiki Kaisha Kobe Seiko Sho**
(Kobe Steel, Ltd.)
Kobe-shi, Hyogo 651-8585 (JP)

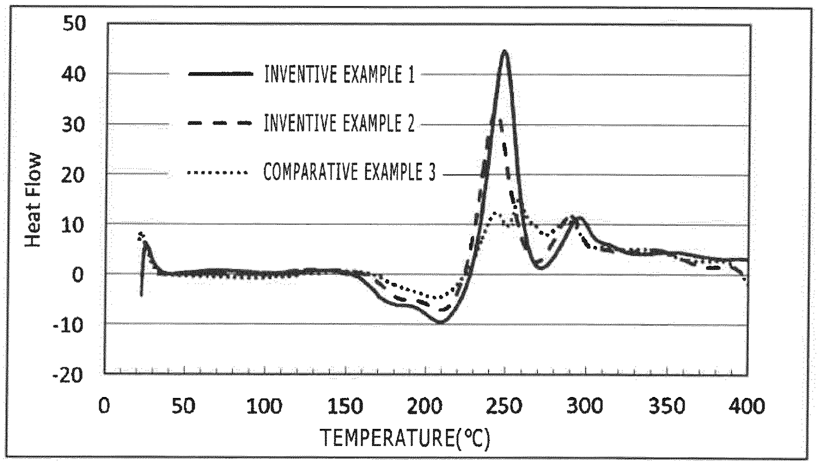
(72) Inventors:
- **SHISHIDO Hisao**
  Tochigi 321-4367 (JP)
- **KITAMURA Tomoyuki**
  Tochigi 321-4367 (JP)

(74) Representative: **Müller-Boré & Partner**
Patentanwälte PartG mbB
Friedenheimer Brücke 21
80639 München (DE)

(54) ALUMINUM ALLOY SHEET AND ALUMINUM ALLOY SHEET MANUFACTURING METHOD

(57) In a differential scanning calorimetric curve of an Al-Mg-Si aluminum alloy sheet with a specific composition in which the total content of Mg and Si is greater than 1.2%, a ratio (B/A) of an endothermic peak within the temperature range of 150-230°C with a height A of 3-10 μW/mg to an exothermic peak within the temperature range of 230°C or above and below 330°C with a height B of 20-50 μW/mg is to be within a specified range.

FIG.1



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Description

Technical Field

[0001] The present invention relates to a 6000-series aluminum alloy sheet manufactured by ordinary rolling and excellent in formability and paint-bake hardenability.

Background Art

[0002] In recent years, out of the consideration for the earth environment and the like, the social requirement of weight reduction of a vehicle body of an automobile is increasing more and more. In order to cope with such a requirement, an aluminum alloy material has been applied to a large body panel (outer panel, inner panel) out of the vehicle body of an automobile in place of steel material such as a steel plate having been used so far.

[0003] For a panel of an outer panel (outer sheet), an inner panel (inner sheet) and the like of a panel structural body such as a hood, a fender, a door, a roof, and a trunk lid out of the large body panel described above, as a thin and high strength aluminum alloy sheet, Al-Mg-Si AA or JIS 6000-series (will be hereinafter simply referred to also as 6000-series) aluminum alloy sheet has been used.

[0004] This 6000-series (Al-Mg-Si) aluminum alloy sheet includes Si and Mg as an indispensable element. Particularly, a 6000-series aluminum alloy of excessive Si type has excellent age-hardenability of the time of the artificial temper aging treatment. Therefore, there is provided the paint-bake hardenability (will be hereinafter referred to also as bake-hard property=BH property and bake-hardenability) securing formability by lowering the proof stress at the time of press forming and bend forming, improving the proof stress even in an artificial temper aging treatment at a comparatively low temperature such as the paint-bake cycle of a panel after forming, and capable of securing a strength required as a panel.

[0005] On the other hand, the outer panel and the like of an automobile are manufactured by combiningly subjecting an aluminum alloy sheet to forming work such as stretch forming in press forming and bend forming as is well known. For example, with respect to a large outer panel such as a hood and a door, a shape of a formed product as an outer panel is obtained by press forming such as stretching, then joining work with an inner panel is executed by hem (hemming) work of a flat hem and the like of the peripheral edge part of the outer panel, and a panel structural body is formed.

[0006] The outer panel and the like of an automobile described above tend to be thinned further for the purpose of the weight reduction, and a high strength so as to be excellent in dent resistance is required in addition to thinning. Accordingly, such artificial temper aging hardenability (paint-bake hardenability) is required more that the proof stress of the aluminum alloy sheet is lowered further to secure the formability at the time of press forming, the aluminum alloy sheet is subjected to age hardening to improve the proof stress by heating at the time of the artificial temper aging treatment at a comparatively low temperature such as the paint-bake cycle of a panel after forming, and capable of securing a required strength even after thinning.

[0007] Conventionally, with respect to the paint-bake hardenability of the 6000-series aluminum alloy sheet as a raw material of such automotive members, to control the Mg-Si clusters has been proposed variously. Also, in recent years, such technologies have been proposed that these Mg-Si clusters are controlled after measuring the Mg-Si clusters by an endothermic peak and an exothermic peak of a differential scanning calorimetric curve (will be hereinafter referred to also as DSC) of the 6000-series aluminum alloy sheet (refer to Patent Literatures 1-5).

[0008] For example, in Patent Literature 1, it is specified that, in the differential scanning calorimetric curve of the 6000-series aluminum alloy sheet, the exothermic peak height W1 in the temperature range of 100-200°C is to be 50 μW or more and the ratio W2/W1 of the exothermic peak height W2 in the temperature range of 200-300°C and the exothermic peak height W1 is to be 20 or less.

[0009] In Patent Literature 2, it is specified that, in the differential scanning calorimetric curve of the 6000-series aluminum alloy sheet, when the exothermic peak height in the temperature range of 230-270°C is denoted by A, the exothermic peak height in the temperature range of 280-320°C is denoted by B, and the exothermic peak height in the temperature range of 330-370°C is denoted by C in the differential scanning calorimetric curve, the exothermic peak height B is to be 20 μW/mg or more, A/B is to be 0.45 or less, and C/B is to be 0.6 or less respectively, A/B and C/B being respective ratios of the exothermic peak heights A, C to the exothermic peak height B.

[0010] In Patent Literature 3, it is specified that, in the differential scanning calorimetric curve of a sheet that is a 6000-series aluminum alloy sheet but with the total amount of Mg and Si being 1.2% or less, only one exothermic peak is to exist or only two exothermic peak with the temperature difference between two peaks being 50°C or less are to exist within the temperature range of 230-330°C, and either the height of the only one exothermic peak or the height of the exothermic peak of one whose peak height is higher out of the only two exothermic peaks is to be in the range of 20-50 μW/mg.

[0011] In Patent Literature 4, it is specified that, in the differential scanning calorimetric curve of a sheet that is a 6000-series aluminum alloy sheet in which to add Sn is essential, as an endothermic peak corresponding to melting of the

MG-Si clusters, the peak height of the endothermic peak within the temperature range of 150-230°C is to be 8 μW/mg or less (but inclusive of 0 μW/mg), whereas as an exothermic peak corresponding to formation of the MG-Si clusters, the peak height of the exothermic peak within the temperature range of 240-255°C is to be 20 μW/mg or more.

[0012] In Patent Literature 5, it is described that, in the differential scanning calorimetric curve after the tempering process including the solution heat treatment and the quenching treatment of an aluminum alloy material, an endothermic peak height of the minus in the temperature range of 150-250°C corresponding to melting of the Si/hole clusters (GPI) is to be 1,000 μW or less, an exothermic peak height of the plus in the temperature range of 250-300°C corresponding to precipitation of the Mg/Si clusters (GPII) is to be 2,000 μW or less, and thereby the aluminum alloy material comes to be excellent in suppressing room temperature aging and in low temperature age-hardenability.

Citation List

Patent Literatures

[0013]

Patent Literature 1: Japanese Patent No. 4117243
Patent Literature 2: Japanese Unexamined Patent Application Publication No. 2013-167004
Patent Literature 3: Japanese Unexamined Patent Application Publication No. 2015-196852
Patent Literature 4: Japanese Unexamined Patent Application Publication No. 2015-196853
Patent Literature 5: Japanese Patent No. 3819263

Summary of Invention

Technical Problems

[0014] However, these conventional technologies for controlling the endothermic peak and the exothermic peak of DSC aim to obtain a high BH property responding to the paint-bake hardening treatment of lowering the temperature and shortening the time for the automotive members described above, and the heating temperature of the paint-bake hardening treatment is 175°C at the highest, and is 150°C in an example on the lower side. In other words, the BH property in the paint-bake hardening treatment at a high temperature such as 180°C or above is not intended.

[0015] Therefore, in order that an Al-Mg-Si aluminum alloy sheet after room temperature aging for a long time was provided with both of an excellent formability and a high BH property in the paint-bake hardening treatment at such a high temperature, there was still room for improvement.

[0016] Further, in obtaining a high BH property also in the paint-bake hardening treatment at the low temperature described above in addition to that both of excellent formability and high BH property in the paint-bake hardening treatment at the high temperature described above were provided, there was still room for improvement.

[0017] That is, in the technological problem of providing all of the elongation, the high temperature BH property, and the low temperature BH property which could be said to be contradictory to each other, there was still room for improvement.

[0018] In view of such circumstances, the object of the present invention is to provide a 6000-series aluminum alloy sheet and a manufacturing method for the same which can provide both of an excellent formability and a high BH property even after room temperature aging for a long time, the high BH property being provided also in the conventional paint-bake hardening treatment at the low temperature described above as well as in the paint-bake hardening treatment at the high temperature described above. Solution to Problem

[0019] In order to solve this problem, the gist of the aluminum alloy sheet of the present invention excellent in formability and paint-bake hardenability is an aluminum alloy sheet containing, in terms of mass%, Mg: 0.3-1.5% and Si: 0.6-1.5% respectively, the total of the Mg content and the Si content being greater than 1.2%, the balance including Al and inevitable impurities, in which, in a differential scanning calorimetric curve of the aluminum alloy sheet, endothermic peaks whose height A is 3-10 μW/mg exist within a temperature range of 150-230°C, exothermic peaks whose height B is 20-50 μW/mg exist within a temperature range of 230°C or above and below 330°C, and a ratio B/A of a maximum peak height B out of the exothermic peaks to a maximum peak height A out of the endothermic peaks is greater than 3.5 and less than 15.0.

[0020] Also, in order to achieve the object described above, the gist of the manufacturing method of an aluminum alloy sheet excellent in formability and paint-bake hardenability of the present invention is that a step of subjecting an aluminum alloy cold rolled sheet to a preliminary temper aging treatment at a low temperature and for a long time is included, the aluminum alloy cold rolled sheet containing, in terms of mass%, Mg: 0.3-1.5% and Si: 0.6-1.5% respectively, the total of the Mg content and the Si content being greater than 1.2%, the balance including Al and inevitable impurities, the preliminary temper aging treatment being for holding the aluminum alloy cold rolled sheet for 5 hours or more and 500 hours or less at the temperature range of 30°C-60°C within one hour after a solution heat treatment and a quenching treatment, and that, in a differential scanning calorimetric curve before the aluminum alloy cold rolled sheet is subjected to an artificial temper aging treatment, endothermic peaks whose height A is 3-10 μW/mg are made to exist within a temperature range of 150-230°C, exothermic peaks whose height B is 20-50 μW/mg are made to exist within a temperature range of 230°C or above and below 330°C, and a ratio B/A of the exothermic peak height B to the endothermic peak height A is made to be greater than 3.5 and less than 15.0.

Advantageous Effects of Invention

[0021] The present inventors studied clusters that could provide both of an excellent formability and a high BH property even after room temperature aging for a long time, the high BH property being provided also in the conventional paint-bake hardening treatment at a low temperature described above as well as in the paint-bake hardening treatment at a high temperature described above.

[0022] As a result, the inventors found that, in order to obtain high elongation even after room temperature aging for a long time, clusters corresponding to the endothermic peak of the mentioned calorimetric curve within the temperature range of 150-230°C were required by a constant degree or more.

[0023] The inventors also found that, even when the bake treatment temperature in the paint-bake hardening treatment might change largely from a high temperature to a low temperature, in order to obtain a high BH amount at any bake treatment temperature, clusters corresponding to the endothermic peak of the mentioned calorimetric curve were to be reduced, or clusters corresponding to the exothermic peak of the temperature range of 230°C-330°C were to be increased.

[0024] That is, the inventors found that high elongation was obtained even after room temperature aging for a long time by precisely controlling the endothermic peak of the mentioned calorimetric curve within the temperature range of 150-230°C and the exothermic peak of the temperature range of 230°C-330°C, and that, even when the bake treatment temperature might change largely from a high temperature to a low temperature, a high BH property was obtained at any bake treatment temperature.

[0025] Further, the inventors found that the differential calorimetric curve for obtaining a high BH property was different particularly according to the temperature of the paint-bake hardening condition (artificial temper aging treatment condition), and also found that, at a comparatively low paint-bake temperature of 175°C or below, it was required to control the differential calorimetric curve more precisely compared to a comparatively high paint-bake temperature of 180°C or above.

[0026] Based on these knowledges, the present invention has allowed a 6000-series aluminum alloy sheet as a raw material of an automotive member to be provided with all of the elongation, the high temperature BH property, and the low temperature BH property which can be said to be contradictory to each other by executing a microstructure control of controlling the differential calorimetric curve more precisely.

Brief Description of Drawing

[0027] Fig. 1 is an explanatory drawing that illustrates a differential scanning calorimetric curve of an aluminum alloy sheet of the present invention.

Description of Embodiments

[0028] The aluminum alloy sheet (formation raw material sheet) referred to in the present invention means a raw material aluminum alloy sheet that is a rolled sheet such as a hot rolled sheet and a cold rolled sheet, is a sheet obtained by subjecting the rolled sheet to tempering (T4) such as a solution heat treatment and a quenching treatment, is before being formed into an automotive member to be used, and is before being subjected to an artificial temper aging treatment (artificial age hardening treatment) such as a paint-bake hardening treatment. In the descriptions below, aluminum is also referred to as Al.

[0029] Below, embodiments of the present invention will be explained specifically according to the requirement.

Aluminum alloy composition:

[0030] First, the chemical composition of the aluminum alloy sheet of the present invention will be explained below including the limiting reason of each element. All of the % indications of the content of each element mean mass%.

[0031] The chemical composition of the aluminum alloy sheet of the present invention is determined to satisfy the formability and the paint-bake hardenability required as a raw material of the automotive members such as the automotive large body panel described above from the composition of the 6000-series aluminum alloy.

[0032] From this viewpoint, the chemical composition of the aluminum alloy sheet of the present invention contains, in terms of mass%, Mg: 0.3-1.5% and Si: 0.6-1.5% respectively, the total of the Mg content and the Si content is greater than 1.2%, and the balance includes Al and inevitable impurities.

[0033] In addition to this composition, one kind or two kinds or more out of Cu: 0.02-0.8%, Fe: 0.05-0.5%, Mn: 0.05-0.3%, Zr: 0.04-0.1%, Cr: 0.04-0.3%, V: 0.02-0.1%, Ag: 0.01-0.1%, and Zn: 0.01-0.3% may be further contained.

Si: 0.6-1.5%

[0034] Si is an indispensable element for forming with Mg temper aging precipitates such as Mg-Si-based precipitates that contribute to solid solution strengthening and improvement of the strength at the time of the artificial temper aging treatment such as the paint-bake treatment to exert the temper aging hardenability, and securing the required strength (proof stress).

[0035] When the Si content is not sufficient, the solid solution Si amount before the paint-bake treatment (before the artificial temper aging heat treatment) reduces, the formation amount of the Mg-Si-based precipitate becomes insufficient, therefore the BH property extremely deteriorates, and the strength becomes insufficient. On the other hand, when the Si content is excessive, coarse crystallized grains and precipitates are formed and the ductility deteriorates which becomes a cause of cracking at the time of rolling a raw material sheet. Therefore, the content of Si is to be made within the range of 0.6-1.5%, preferably within the range of 0.7-1.5%.

Mg: 0.3-1.5%

[0036] Mg is also an indispensable element for forming with Si temper aging precipitates such as Mg-Si-based precipitates that contribute to solid solution strengthening and improvement of the strength at the time of the artificial temper aging treatment such as the paint-bake treatment to exert the temper aging hardenability, and securing the required strength. When the Mg content is not sufficient, the solid solution Mg amount before the paint-bake treatment reduces, the formation amount of the Mg-Si-based precipitate becomes insufficient, therefore the BH property extremely deteriorates, and the strength becomes insufficient. On the other hand, when the Mg content is excessive, a shearing band is liable to be formed at the time of cold rolling which becomes a cause of cracking at the time of rolling a raw material sheet. Therefore, the content of Mg is to be made within the range of 0.3-1.5%, preferably within the range of 0.4-0.8%.

[0037] Also, in order to exert excellent artificial temper aging hardenability in the paint-bake treatment after formation into a panel, the total of the Mg content and the Si content is to be made greater than 1.2%. When this total is 1.2% or less as in Patent Literature 3 described above, even when the manufacturing condition of the sheet may be within the preferable range described below, the endothermic peak and the exothermic peak specified in the present invention cannot be formed, the artificial temper aging hardenability becomes insufficient, and the required strength cannot be secured. However, the upper limit of the total of the Mg content and the Si content is determined by a limit at which the sheet can be manufactured without causing a hot rolling crack, and is to be preferably made 2.5%.

One kind or two kinds or more selected from Cu, Fe, Mn, Zr, Cr, V, Ag, and Zn

[0038] These elements can be deemed to be elements having the same effect in the present invention because they commonly have an effect of high strengthening a sheet, and are to be contained selectively according to the necessity, however, it is a matter of course that there is a common part and a different part in the concrete mechanism of it.

[0039] Cu can improve the strength by solid solution strengthening. The effect is small when the content of Cu is not sufficient. Even when the content of Cu is excessive, the effect saturates, and corrosion resistance and the like are deteriorated to the contrary.

[0040] Fe plays the roles of forming crystallized grains, becoming nuclei of the recrystallized grains, preventing the grains from being coarsened, and improving the strength. The effect is small when the content is not sufficient. When the content is excessive, Fe forms a coarse compound and becomes an origin of breakage, and the strength and the formability deteriorate.

[0041] Mn, Zr, Cr, and V miniaturize the grain of the slab and the final sheet product, and contribute to improvement of the strength. Further, these elements exist as the dispersed particles, contribute to miniaturization of the grains, and also improve the formability. When the content of each element is not sufficient, the effect of improving the strength and the formability by the miniaturization of the grains becomes insufficient. On the other hand, when these elements are excessive, a coarse compound is formed, and the ductility is deteriorated.

[0042] Ag has effects of positively and finely precipitating temper aging precipitates that contribute to improvement of the strength by the artificial temper aging heat treatment after forming work into an automotive member, and promoting high strengthening. When the content is not sufficient, the strength improving effect is small. When the content is excessive, various properties such as the rollability and the weldability are deteriorated to the contrary, the strength improving effect saturates, and the cost increases.

[0043] Zn is useful in improving the artificial temper aging hardenability (BH property), and has an effect of promoting precipitation of a compound phase of the GP zone and the like into the grain of the sheet microstructure and increasing the strength in the paint-bake treatment.

[0044] Therefore, when these Cu, Fe, Mn, Zr, Cr, V, Ag, and Zn are to be contained, as described above, one kind or two kinds or more is to be contained in the range of Cu: 0.02-0.8%, Fe: 0.05-0.5%, Mn: 0.05-0.3%, Zr: 0.04-0.1%, Cr: 0.04-0.3%, V: 0.02-0.1%, Ag: 0.01-0.1%, and Zn: 0.01-0.3%.

Other elements

[0045] Other elements such as Ti and B other than those described above are inevitable impurities. Ti forms coarse compounds with B and deteriorates the mechanical property. However, since there is also an effect of miniaturizing the grain of an aluminum alloy slab by being contained in a minute amount, containment of each element within a range specified in JIS Standards and the like as the 6000-series alloy is allowed. As an example of this allowable amount, Ti is to be made 0.1% or less, preferably 0.05% or less. B is to be made 0.03% or less. In the meantime, in the present invention, Sn that is made indispensable in Patent Literature 4 described above is not added. When Sn is added, in a case of employing the preferable manufacturing condition of a sheet described below, it is possible that the Mg-Si clusters are reduced to the contrary, the endothermic peak and the exothermic peak specified in the present invention cannot be formed, the artificial temper aging hardenability becomes insufficient, and the required strength cannot be secured.

(Raw material sheet microstructure)

[0046] On the premises of the alloy compositions described above, in the present invention, the microstructure of the aluminum alloy sheet is defined by DSC (differential scanning calorimetric curve: DSC profile) obtained by a differential scanning thermal analysis as an indicator that indicates beforehand the existence state of the artificial temper aging precipitate in the member in which this sheet is used as a raw material.

[0047] That is, the present invention is defined by DSC (differential scanning calorimetric curve: DSC profile) obtained by a differential scanning thermal analysis in order to be provided with both of an excellent formability and a high BH property even in a paint-bake hardening treatment at a comparatively low temperature as well as a high BH property in a paint-bake hardening treatment at a comparatively high temperature which is the main object even after the temper aging at a room temperature for a long time.

[0048] In a paint-bake condition at a comparatively low temperature, when an endothermic peak within the temperature range of 150-230°C exists, a high BH amount is hardly obtained. However, in a paint-bake condition at a comparatively high temperature which is the main object of the present invention, even when the endothermic peak may exist to a certain degree, a high BH amount is obtained. In a conventional paint-bake condition at a comparatively low temperature, it is presumed that a high BH property is not obtained because, even when clusters corresponding to the endothermic peak described above may be molten during the paint-bake treatment, a strengthening phase thereafter is less likely to be newly formed.

[0049] On the other hand, in a paint-bake condition at a comparatively high temperature which is the main object of the present invention, it is presumed that, since clusters corresponding to the endothermic peak described above are molten within an extremely short time and a strengthening phase is newly formed thereafter easily, a high BH property is secured even when the endothermic peak described above may exist beforehand. Therefore, in a paint-bake hardening condition at a comparatively high temperature which is the main object of the present invention, the endothermic peak described above can be made high, and the work hardenability can be enhanced by existence of the clusters corresponding to this endothermic peak. Accordingly, when the exothermic peak within the temperature range of 230°C or above and below 330°C where a BH property is enhanced is made to exist as well, both of high work hardenability (formability) and BH property can be achieved.

[0050] This paint-bake hardening treatment condition at a comparative high temperature means a paint-bake hardening treatment under a condition of the heating temperature of 180-230°C and the heating holding time of 10-30 minutes for example, and is differentiated in terms of the heating temperature in particular from 175°C at highest of the heating temperature of the conventional paint-bake hardening treatment of comparatively low temperature and short time.

[0051] When both of these exothermic peak and endothermic peak are to be made to exist, in addition to each of the peak heights, the balance of both of the peak heights also becomes important. For example, when the ratio of exothermic peak/endothermic peak is too small, either the existence of the clusters corresponding to the endothermic peak is too large and the BH property become too low, or the exothermic peak is too low, clusters becoming the strengthening phase are excessive, and the elongation deteriorates. On the other hand, when exothermic peak/endothermic peak is too large, either the existence of the clusters corresponding to the endothermic peak is too small and the work hardenability is inferior, or the exothermic peak is too high, the amount of clusters becoming the strengthening phase is not sufficient, and the BH property excessively deteriorates.

[0052] Based on such knowledges, in the present invention, in order to achieve both of high elongation and the BH property at a comparatively high temperature, in DSC before the aluminum alloy sheet is subjected to an artificial temper aging treatment, an endothermic peak whose height A is 3-10 μW/mg is to exist within a temperature range of 150-230°C, an exothermic peak whose height B is 20-50 μW/mg is to exist within a temperature range of 230°C or above and below 330°C, and a ratio B/A of the exothermic peak height B and the endothermic peak height A is to be greater than 3.5 and less than 15.0.

[0053] Further, in order to achieve both of the high elongation and the BH property at a comparatively low temperature in addition to a case of a comparatively high temperature described above, in DSC before the aluminum alloy sheet is subjected to an artificial temper aging treatment, an endothermic peak whose height A is preferably 3-8 μW/mg is to exist within a temperature range of 150-230°C, an exothermic peak whose height B is preferably 20-40 μW/mg is to exist within a temperature range of 230°C or above and below 330°C, and a ratio B/A of the exothermic peak height B and the endothermic peak height A is to be greater than 3.5 and less than 15.0. Furthermore, it is more preferable that the height A of the endothermic peak is 3-7 μW/mg, and the height B of the exothermic peak is 20-35 μW/mg.

[0054] With respect to the endothermic peak described above, the fact that an endothermic peak is high on the minus side means that the clusters are molten during the differential thermal analysis, and, in other words, means that there are many clusters that correspond to the endothermic peak. When the height A of the peak on the minus side is as low as less than 3 μW/mg, the work hardenability deteriorates, and the formability deteriorates. On the other hand, when the height A of the peak on the minus side becomes too high beyond 10 μW/mg, the BH property at a comparatively high temperature deteriorates. When the height A of the peak on the minus side becomes too high beyond 7 μW/mg, the BH property at a comparatively low temperature deteriorates.

[0055] With respect to the exothermic peak described above, the fact that an exothermic peak is high means that many clusters becoming the strengthening phase or the nuclei of the strengthening phase are generated during the differential thermal analysis, and, in other words, means that there are not many clusters becoming the strengthening phase or the nuclei of the strengthening phase. When the height B of the exothermic peak is too high beyond 50 μW/mg, the amount of the clusters becoming the strengthening phase or the nuclei of the strengthening phase is not sufficient, and the BH property of the paint-bake hardening at a comparatively high temperature deteriorates. When the height B of the peak on the plus side is too high beyond 40 μW/mg, the BH property of the paint-bake hardening at a comparatively low temperature deteriorates. On the other hand, when the height B of the peak on the plus side is as low as less than 20 μW/mg, there are excessive clusters becoming the strengthening phase or the nuclei of the strengthening phase, and the elongation deteriorates. Incidentally, these tendencies are on the premises that the alloy composition of the sheet satisfies the range of the present invention.

[0056] Thus, the microstructure defined by DSC at the stage of the raw material sheet is correlated very well to the generation behavior of the precipitated phase at the time of the artificial temper aging treatment (the time of BH) of a member such as the automotive panel described above manufactured from this raw material sheet. As a result, instead of manufacturing the member described above purposely, when the DSC described above is controlled at the stage of this raw material sheet, the formability and the BH property of this raw material sheet can be evaluated. In other words, the microstructure defined by the DSC described above at the stage of this raw material sheet possibly becomes an indicator of the formability and the BH property in a member in which this raw material sheet is used as a formation raw material.

[0057] For example, in Patent Literature 1 described above, there is no endothermic peak whose height is 3-10 μW/mg within the temperature range of 150-230°C, whereas the exothermic peak exists within the temperature range of 100-200°C. In Patent Literature 2 described above, as illustrated in Fig. 1 thereof, there is no endothermic peak whose height is 3-10 μW/mg within the temperature range of 150-230°C. In Patent Literature 3 described above, the total amount of Mg and Si is 1.2% or less, the endothermic peak and the exothermic peak specified in the present invention cannot be formed, the artificial temper aging hardenability becomes insufficient, and the required strength cannot be secured. In Patent Literature 4 described above, as illustrated in Fig. 1 thereof, there is no endothermic peak whose height is 3-10 μW/mg within the temperature range of 150-230°C, and the exothermic peak whose height exceeds 20 μW/mg exists within the temperature range of above 260°C and 330°C or below. In Patent Literature 5 described above, as illustrated in Fig. 1 thereof, the endothermic peak whose height is 3-10 μW/mg exists within the temperature range of 150-230°C, the exothermic peak exists at the position of 260°C, however the ratio of the exothermic peak/the endothermic peak is less than 3.5 which is too small, and the rate of the endothermic peak is too high.

[0058] Therefore, these conventional technologies for controlling the endothermic peak and the exothermic peak of DSC cannot achieve both of the high elongation (formability) and the paint-bake hardenability of the 6000-series aluminum alloy sheet after the temper aging at a room temperature for a long time in the paint-bake hardening condition at a comparatively high temperature which is the object of the present invention differently from the technology for controlling the endothermic peak and the exothermic peak of DSC specified in the present invention.

(Method for controlling microstructure specified by DSC)

[0059] As described below, control of the microstructure determined by the exothermic peak of DSC described above is executed by performing a preliminary temper aging treatment at a low temperature and for a long time of holding the aluminum alloy cold rolled sheet for 5 hours or more and 500 hours or less in the temperature range of 30°C-60°C within one hour after the solution treatment and the quenching treatment.

[0060] Also, as described below, in order to enhance the BH property at a comparatively low temperature, after performing a preliminary temper aging treatment at a high temperature and for a short time of holding for 5 seconds or more and 300 seconds or less in the temperature range of 100°C-300°C within one hour after the solution heat treatment and the quenching treatment described above, the processes up to the preliminary temper aging treatment described above are performed. Therefore, there is an advantage of being capable of controlling without largely changing the 6000-series aluminum alloy composition already standardized as the automotive member described above of the rolled sheet, and without largely changing the rolling steps according to an ordinary method.

(Manufacturing method)

[0061] The 6000-series aluminum alloy sheet of the present invention is a cold rolled sheet obtained by that a slab is hot rolled after a soaking treatment and is further cold rolled, and is manufactured by an ordinary method in which tempering such as a solution heat treatment is further performed. That is, such an aluminum alloy hot rolled sheet is obtained that is manufactured through respective ordinary manufacturing steps of casting, homogenization, and hot rolling, and has the sheet thickness of approximately 2-10 mm. Then, cold rolling is performed to obtain a cold rolled sheet with the sheet thickness of 3 mm or less.

(Melting, casting)

[0062] First, in the melting and casting step, the molten metal of an aluminum alloy having been meltingly adjusted to within the 6000-series composition range described above is casted properly by selecting an ordinary melting casting method such as a continuous casting method, and a semi-continuous casting method (DC casting method). Here, in order to control the clusters into the specified range of the present invention, it is preferable that the average cooling rate at the time of casting is increased (made fast) as much as possible to 30°C/min or more from the liquid phase line temperature to the solid phase line temperature. When such a temperature (cooling rate) control in the high temperature region in casting is not performed, the cooling rate at this high temperature region inevitably becomes slow. Then, the amount of the crystallized grain formed to be coarse in the temperature range at this high temperature region increases, and dispersion of the size and the amount of the crystallized grain in the plate width direction and the thickness direction of the slab also becomes large. As a result, it becomes highly possible that the DSC described above cannot be controlled to the range of the present invention.

[0063] Then, the aluminum alloy slab having been casted as described above is subjected to homogenization prior to hot rolling. This homogenization (soaking treatment) is important for sufficiently dissolving Si and Mg in addition to homogenizing the microstructure (eliminating the segregation within the grain in the microstructure of the slab) which is an ordinary object.

[0064] The homogenization temperature and the homogenization (holding) time are properly selected from the range of 500°C or above and 580°C or below, and one hour or more respectively, and Si and Mg are sufficiently dissolved. When this homogenization temperature is low, the solid solution amount of Si and Mg cannot be secured, and the specified exothermic peak of DSC described above cannot be achieved even by the preliminary temper aging treatment (reheating treatment) after the solution heat treatment/quenching treatment described below. Also, the segregation within the grain cannot be eliminated sufficiently, the segregation acts as an origin of breakage, and therefore the formability deteriorates.

[0065] Although hot rolling is performed after this homogenization is performed, it is preferable not to lower the temperature of the slab to 450°C or below until the start of the hot rough rolling after the homogenization, and to secure the solid solution amount of Si and Mg. When the temperature of the slab lowers to 450°C or below by the start of the rough rolling, it becomes highly possible that Si and Mg precipitate and the solid solution amount of Si and Mg for achieving the specified DSC described above cannot be secured.

(Hot rolling)

[0066] The hot rolling is configured of the rough rolling step and the finish rolling step of the slab according to the plate thickness to be rolled. In these rough rolling step and finish rolling step, a rolling machine of the reverse type, the tandem type, and the like are used appropriately.

[0067] During rolling from the start to finish of the hot rough rolling, it is required not to lower the temperature to 400°C or below and to secure the solid solution amount of Si and Mg. When the temperature of the rough rolled sheet lowers to 400°C or below during the hot rough rolling, it becomes highly possible that Si and Mg precipitate and the solid solution amount of Si and Mg for achieving the specified DSC described above cannot be secured.

[0068] After such hot rough rolling, hot finish rolling with the finishing temperature being made within the range of 250-360°C is performed. When the soaking temperature described above and the finishing temperature of this finish rolling are too low, Mg- and Si-based compound is formed during soaking and hot rolling, the balance of solid solution Mg/Si changes, and it becomes hard to obtain the specified DSC described above.

(Annealing of hot rolled sheet)

[0069] Annealing before cold rolling of this hot rolled sheet is not necessary, but may be performed.

(Cold rolling)

[0070] In cold rolling, the hot rolled sheet described above is rolled, and is manufactured into a cold rolled sheet (including also a coil) having a desired final sheet thickness. However, in order to further miniaturize the grain, it is preferable that the cold rolling ratio is 60% or more, and intermediate annealing may be performed between the cold rolling passes with an aim similar to that of the annealing described above.

(Solution heat treatment and quenching treatment)

[0071] After the cold rolling, the solution heat treatment and the subsequent quenching treatment to the room temperature are performed. With respect to this solution heat treatment, in order to secure sufficient solid solution amount of each element such as Mg and Si, heating to the solution heat treatment temperature of 500°C or above and the melting temperature or below is preferable.

[0072] Also, from the viewpoint of suppressing formation of the coarse grain boundary compound that deteriorates the formability, it is desirable that the average cooling rate from the solution heat treatment temperature to the quenching finish temperature that is the room temperature is made 20°C/s or more. When the average cooling rate of the quenching treatment to the room temperature after the solution heat treatment is low, coarse Mg_2Si and the single body Si are formed during cooling, and the bending workability deteriorates. In addition, the solid solution amount after the solution heat treatment reduces, and the BH property deteriorates. In order to secure this cooling rate, in the quenching treatment, air cooling such as a fan, water cooling means and conditions such as the mist, spray, and immersion are respectively selected and used.

(Preliminary temper aging treatment: reheating treatment)

[0073] It is preferable to perform a quenching treatment after such a solution heat treatment and cooling to the room temperature, and to subject the cold rolled sheet to a preliminary temper aging treatment (reheating treatment) within one hour thereafter. In order to control the microstructure having been determined by the peak of DSC described above, it is preferable that this preliminary temper aging treatment is executed by performing a preliminary temper aging treatment at a low temperature for a long time for the holding of 5 hours or more and 500 hours or less in the temperature range of 30°C-60°C which are a lower temperature and a longer time compared to the ordinary method. Thereby, the microstructure formed with Mg-Si clusters having excellent balance of Mg and Si and determined by the peaks of DSC described above is obtained. Therefore, by the preliminary temper aging treatment at a low temperature for a long time, both of the high elongation and the BH property at a comparatively high temperature can be provided.

[0074] When the room temperature holding time after finishing the quenching treatment to the room temperature until the start of the preliminary temper aging treatment (the start of heating) is too long, because of the room temperature temper aging, the clusters corresponding to the endothermic peak are excessively formed and the BH property is liable to deteriorate. Therefore, this room temperature holding time is preferable to be as short as possible, the solution heat treatment and quenching treatment and the reheating treatment may be continuous so as to almost eliminate the time difference between them, and the time of the lower limit is not set particularly.

[0075] When the preliminary temper aging temperature described above is below 30°C or the holding time is less than 5 hours, the case becomes similar to the case of not performing this preliminary temper aging treatment, the clusters corresponding to the endothermic peak are excessively formed and the BH property is liable to deteriorate. On the other hand, when the preliminary temper aging condition described above exceeds 60°C or exceeds 500 hours, the formation amount of the clusters that become the strengthening phase corresponding to the exothermic peak and the nuclei of the strengthening phase becomes excessive, the strength in the press forming before the paint-baking becomes too high, and the formability is liable to deteriorate.

[0076] Here, in order to further enhance the BH property at a comparatively low temperature, it is preferable to perform firstly the processes up to the preliminary temper aging treatment at a high temperature for a short time for the holding of 5 seconds or more and 300 seconds or less in the temperature range of 100°C-300°C within one hour after the solution heat treatment and quenching treatment described above, and to perform immediately thereafter the preliminary temper aging treatment at a low temperature for a long time described above. Thereby, the control of DSC by the preliminary temper aging treatment at a low temperature for a long time described above can be made positive, and the endothermic peak height A within the temperature range of 150-230°C in DSC can be controlled to a preferable range of 3-8 μW/mg, and to a more preferable range of 3-7 μW/mg. In a similar manner, the exothermic peak height B within the temperature range of 230°C or above and below 330°C in DSC can be controlled to a preferable range of 20-40 μW/mg and to a more preferable range of 20-35 μW/mg. When this preliminary temper aging treatment at a high temperature for a short time is not performed or when the conditions described above are not satisfied even if this preliminary temper aging treatment at a high temperature for a short time is performed, according to the alloy composition and the manufacturing history, it is possible that the microstructure determined by the peaks of DSC described above cannot be achieved, or that the BH property at a comparatively low temperature deteriorates.

[0077] Thus, the aluminum alloy sheet of the present invention manufactured to have the microstructure determined by the peaks of DSC described above is press formed into a large body panel and the like of an automobile and the like as a raw material, is painted then, and is thereafter subjected to the paint-bake hardening treatment (artificial temper aging treatment) to be high strengthened. As described above, in order to achieve the effects of the present invention, this paint-bake hardening treatment is preferable to be performed under a high temperature, and the conditions of the heating temperature of 180-230°C and the heating holding time of 10-30 minutes are exemplified. When the heating temperature is too low and so on deviating from this paint-bake hardening treatment condition, the microstructure expressed by the differential calorimetric curve is required to be controlled more precisely as described above.

[Examples]

[0078] Next, examples of the present invention will be explained. The 6000-series aluminum alloy sheets having different microstructure specified by DSC of the present invention were manufactured by separately changing the composition and the manufacturing condition. The As proof stress (the proof stress before the paint-bake hardening treatment), the AB proof stress (the proof stress after the paint-bake hardening treatment), the breaking elongation, and the BH property (the paint-bake hardenability) after the holding for 100 days at the room temperature after manufacturing the sheet were respectively measured and evaluated. These results are illustrated in Tables 1, 2.

[0079] In the concrete method for the dividing manufacturing described above, the preliminary temper aging treatment condition after the 6000-series aluminum alloy sheets having the composition illustrated in Table 1 were subjected to the solution heat treatment and quenching treatment was changed variously as illustrated in Table 2. Here, in the indication of the content of each element in Table 1, the indication where the numerical value in each element is blank expresses that the content is the detectable limit or less.

(Manufacturing condition of aluminum alloy sheet)

[0080] The concrete manufacturing condition of the aluminum alloy sheet were made common (the same) for each example as described below with the exception of the preliminary temper aging treatment condition described above. The aluminum alloy slabs having each composition illustrated in Table 1 were smelted commonly by the DC casting method. At this time, commonly to each example, the average cooling rate in casting was made 50°C/min from the liquid phase line temperature to the solid phase line temperature. Subsequently, the slab after being subjected to surface scalping according to the necessity was subjected to the soaking treatment by 550°C×10 hours, hot rough rolling was thereafter started at the temperature, and hot finishing rolling whose finishing temperature was between 250°C and 360°C was thereafter performed to obtain a hot rolled sheet. This hot rolled sheet was cold rolled with the working rate of 67% to obtain a cold rolled sheet with the thickness of 1.0 mm.

[0081] Further, each of these cold rolled sheets was subjected to the solution heat treatment for 1 minute at 550°C using a nitric furnace, and was thereafter cooled to the room temperature by performing water cooling. Within one hour after this cooling, preliminary temper aging at a high temperature for a short time using an oil bath and preliminary temper aging at a low temperature for a long time using an atmospheric furnace were performed by the temperature (°C) and the holding time (hr) illustrated in Table 2, and air cooling was performed after the preliminary temper aging treatment.

[0082] From each final product sheet after room temperature standing for 100 days after these temper treatments, sample sheets (blanks) 300 mm×300 mm were cut out from the end part in the longitudinal direction and the center part in the width direction of the product, and DSC described above and the property of each sample sheet were measured and evaluated. These results are illustrated in Table 2.

(Measurement of DSC)

[0083] DSC described above of the microstructure at three positions in the center part in the sheet width direction of the sample sheet was measured, and the temperature (°C) and the height (μW/mg) of the endothermic peak and the temperature (°C) and the height (μW/mg) of the exothermic peak were measured respectively in DSC (differential scanning calorimetric curve) of this sheet by the average value of these three positions. In Table 2 that illustrates this result, for the convenience purpose, the endothermic peak within the temperature range of 150-230°C is simply expressed as "endothermic peak" and the exothermic peak within the temperature range of 230°C or above and below 330°C is simply expressed as "exothermic peak".

[0084] In the differential thermal analysis at each measuring position of these sample sheets described above, DSC was measured respectively with the same condition of; test apparatus: TG/DTA 6300 made by Seiko Instruments Inc., standard substance: aluminum, sample container: aluminum, temperature raising condition: 10°C/min, atmosphere: argon (50 ml/min), and sample weight: 39.0-41.0 mg, the profile (μW) of the differential thermal analysis having been obtained was divided by the sample weight (μW/mg), and the endothermic height and the exothermic height from a reference level were thereafter measured, a region where the profile of the differential thermal analysis becomes horizontal in the section of 0-100°C in the differential thermal analysis profile described above being made the reference level of 0.

Paint-bake hardenability

[0085] As the mechanical property of the sample sheet described above, the 0.2% proof stress (As proof stress) and the breaking elongation (%) were obtained by a tensile test. The 0.2% proof stress (AB proof stress) of the sample sheet after each of these sample sheets was subjected to stretching of 2% which simulated the press forming into the automotive member described above and was thereafter subjected to respective artificial temper aging hardening treatments of 185°C×20 min as the paint-bake hardening treatment at a high temperature and 170°C×20 min as the paint-bake hardening treatment at a low temperature respectively commonly to each sample sheet (after BH) was obtained by a tensile test. Further, with respect to the 0.2% proof stress after BH evaluating the BH property of each sample sheet from the difference of the 0.2% proof stress of them (the increment of the proof stress), 190 MPa or more was evaluated to have passed in the paint-bake hardening treatment at a high temperature (185°C×20 min), and 160 MPa or more at the lowest and preferably 180 MPa or more were evaluated to have passed in the paint-bake hardening treatment at a low temperature (170°C×20 min). With respect to the breaking elongation that corresponds to the evaluation of the press formability, 25% or more was evaluated to have passed. Also, with respect to the breaking elongation that corresponds to the evaluation of the press formability, the difference of only 1% of 24% and 25% largely affects, for example, to whether or not the corner part and the outer line of the outer panel of an automobile where the shape is sharpened or complicated can be formed with a beautiful and sharp curved surface configuration without distortion and a wrinkle.

[0086] With respect to the tensile test described above, No. 13-A test specimen (20 mm×80 mm GL×sheet thickness) of JIS Z 2201 was taken from each of the sample sheets described above respectively, and the tensile test was performed at the room temperature. The tensile direction of the test specimen at this time was made the direction orthogonal to the rolling direction. The tensile rate was made 5 mm/min up to the 0.2% proof stress, and 20 mm/min at the proof stress and onward. The mechanical property was measured with the N-number of 5, and was calculated by the average value respectively. With respect to the test specimen for measuring the proof stress after BH described above, the BH treatment described above was performed after applying the pre-strain of 2% to this test specimen by this tensile test machine.

[0087] As illustrated in Tables 1, 2 respectively, the inventive examples 1-8 have been manufactured within the composition range of the present invention and in the preferable condition range, and have been subjected to the preliminary temper aging treatment at a low temperature for a long time in the preferable range. Therefore, each of these inventive examples conforms to what is specified in the present invention in terms of DSC as illustrated in Table 2, and are excellent in the formability and the BH property as illustrated in Table 2 even after the room temperature temper aging for a long period.

[0088] Specifically, the inventive examples 1-8 have a high breaking elongation of 26% or more at the lowest, the BH property of a high temperature (185°C×20 min) of 192 MPa or more at the lowest, and the BH property of a low temperature (170°C×20 min) of 162 MPa or more at the lowest.

[0089] In addition, in comparison between the inventive examples of Table 2, in the inventive example 2 in which the preliminary temper aging treatment at a high temperature and for a short time is performed and the preliminary temper aging treatment at a low temperature and for a long time described above is performed immediately thereafter, the BH property at a comparatively low temperature has become high compared to the inventive example 1 in which the preliminary temper aging treatment at a high temperature and for a short time is not performed and only the preliminary temper aging treatment at a low temperature and for a long time is performed. In a similar manner, in the inventive examples 6, 7, and 8 in which the preliminary temper aging treatment at a high temperature and for a short time is performed and the preliminary temper aging treatment at a low temperature and for a long time described above is performed immediately thereafter, the BH property at a comparatively low temperature has become high in average possibly depending on the alloy composition compared to the inventive examples 3, 4, and 5 in which the preliminary temper aging treatment at a high temperature and for a short time is not performed and only the preliminary temper aging treatment at a low temperature and for a long time is performed.

[0090] This is because, in the inventive examples 2, 6, 7, and 8, the preliminary temper aging treatment at a high temperature and for a short time is further added, the height A of the endothermic peak within the temperature range of 150-230°C in DSC has been capable of being controlled more precisely to the preferable range (3-8 μW/mg) and the more preferable range (3-7 μW/mg), and the height B of the exothermic peak within the temperature range of 230°C or above and below 330°C in DSC has been capable of being controlled more precisely to the preferable range (20-40 μW/mg) and the more preferable range (20-35 μW/mg) in a similar manner.

[0091] On the other hand, the comparative examples 1-6 of Table 2 use the alloy example 1 that is the same as the inventive example. However, as illustrated in Table 2, in each of these comparative examples, the manufacturing conditions such as the temperature and the holding time of the preliminary temper aging treatment deviate from the preferable condition. As a result, DSC deviates from the range specified in the present invention, either the BH property or the formability after the room temperature temper aging for a long period is inferior compared to the inventive example 1 that has the same alloy composition, and it has not been possible to have both of the BH property and the formability. Specifically, either the BH property at a high temperature (185°C×20 min) has become less than 190 MPa even when the breaking elongation is 26% or more, or the breaking elongation has become less than 25% even when the BH property at a high temperature (185°C×20 min) is 190 MPa or more, and the acceptance criteria described above have not been satisfied.

[0092] Among them, in the comparative example 1, the preliminary temper aging treatment is not performed. Therefore, even though the endothermic peak exists within the temperature range of 150-230°C, the height A of the endothermic peak exceeds 10 μW/mg and is too high, and the height B of the exothermic peak within the temperature range of 230°C or above and below 330°C also exceeds 50 μW/mg and is too high.

[0093] In the comparative example 2, the time of the preliminary temper aging treatment on the low temperature side is too short. Therefore, even though the endothermic peak exists within the temperature range of 150-230°C, the height A of the endothermic peak exceeds 10 μW/mg and is too high, and the height B of the exothermic peak within the temperature range of 230°C or above and below 330°C also exceeds 50 μW/mg and is too high.

[0094] In the comparative example 3, the temperature of the preliminary temper aging treatment on the low temperature side is too high. Therefore, even though the endothermic peak with the height A of 3-10 μW/mg exists within the temperature range of 150-230°C, the height B of the exothermic peak within the temperature range of 230°C or above and below 330°C is less than 20 μW/mg and is too low.

[0095] In the comparative example 4, the time of the preliminary temper aging treatment on the low temperature side is too long. Therefore, even though the endothermic peak exists within the temperature range of 150-230°C, the height A of the endothermic peak is less than 3 μW/mg and is too low, and also the height B of the exothermic peak within the temperature range of 230°C or above and below 330°C is less than 20 μW/mg and is too low.

[0096] In the comparative example 5, the time of the preliminary temper aging treatment on the high temperature side is too long. Therefore, even though the endothermic peak exists within the temperature range of 150-230°C, the height A of the endothermic peak is less than 3 μW/mg and is too low, and also the height B of the exothermic peak within the temperature range of 230°C or above and below 330°C is less than 20 μW/mg and is too low.

[0097] In the comparative example 6, the temperature of the preliminary temper aging treatment on the low temperature side is too high. Therefore, even though the endothermic peak exists within the temperature range of 150-230°C, the height A of the endothermic peak is less than 3 μW/mg and is too low, and the ratio B/A to the height B of the exothermic peak within the temperature range of 230°C or above and below 330°C exceeds 15.0 and is too large.

[0098] Even though the comparative examples 7 and 8 of Table 2 are manufactured in the preferable range including the preliminary temper aging treatment condition described above, the alloy numbers 7 and 8 of Table 1 are used respectively, and the alloy compositions deviate from the range of the present invention respectively. Therefore, as a result, as illustrated in Table 2, in these comparative examples, DSC and the like deviate from the range specified in the present invention, either the BH property or the formability after the room temperature temper aging for a long period is inferior compared to the inventive example, and it has not been possible to have both of the BH property and the formability. Specifically, even though the breaking elongation is 25% or more, the BH property at a high temperature (185°C×20 min) is approximately 138-146 MPa at the most, and the BH property at a low temperature (170°C×20 min) is approximately 133-139 MPa at the most.

[0099] The comparative example 7 is formed of the alloy 7 of Table 1, the amount of Mg is too small, and also the amount of the total content of Mg and Si is too small. Therefore, even though the endothermic peak exists within the temperature range of 150-230°C, the height A of the endothermic peak is less than 3 μW/mg and is too low, and also the height B of the exothermic peak within the temperature range of 230°C or above and below 330°C is less than 20 μW/mg and is too low.

[0100] The comparative example 8 is formed of the alloy 8 of Table 1, the amount of Si is too small, and also the total content of Mg and Si is too small. Therefore, even though the endothermic peak exists within the temperature range of 150-230°C, the height A of the endothermic peak is less than 3 μW/mg and is too low, and the height B of the exothermic peak within the temperature range of 230°C or above and below 330°C is also less than 20 μW/mg and is too low.

[0101] DSC selected from these inventive examples and comparative examples is illustrated in Fig. 1. In Fig. 1, the unit of the vertical axis written as "Heat Flow" is μW/m, the bold solid line represents the inventive example 1 of Table 2, the bold dotted line (broken line) represents the inventive example 2, and the narrow dotted line represents the comparative example 3. As Fig. 1 shows, in these inventive examples, the endothermic peak whose height A is 3-10 μW/mg exists within the temperature range of 150-230°C, the exothermic peak whose height B is 20-50 μW/mg exists within the temperature range of 230°C or above and below 260°C, and the exothermic peak whose height is 20 μW/mg or more does not exist in the temperature range of 260°C or above and below 330°C.

[0102] From the result of the examples described above, the critical significance of the composition and each condition of DSC specified in the present invention in order to be provided with both of the excellent formability and the high BH property even after the room temperature temper aging for a long time and with the paint-bake hardening treatment at a high temperature is confirmed.

[Table 1]

Alloy No.	Chemical composition of Al-Mg-Si alloy sheet (mass%, balance is Al)										
	Mg	Si	Mg+Si	Fe	Mn	Cu	Cr	Zr	V	Zn	Ag
1	0.59	1.01	1.60	0.22	0.09						
2	0.41	0.96	1.37	0.20	0.09	0.1					
3	0.48	0.78	1.26	0.22	0.1	0.7					
4	0.54	0.97	1.51	0.21	0.11			0.05		0.2	
5	0.50	1.01	1.51	0.20	0.1		0.2				
6	0.74	0.67	1.41	0.19	0.1		0.05		0.06		0.07
7	0.22	0.96	1.18	0.18	0.09						
8	0.59	0.35	0.94	0.22	0.11						

＊The field where the numerical value in each element is blank means that the content is the detectable limit or less.

[Table 2]

Classification	No.	Alloy No. of Table 1	Preliminary temper aging at high temperature and for short time		Preliminary temper aging at low temperature and for long time		Aluminum alloy sheet microstructure after holding at room temperature for 100 days			Aluminum alloy sheet property after holding at room temperature for 100 days					
			Temperature (°C)	Time (sec)	Temperature (°C)	Time (hour)	Endothermic peak height A (μW/mg)	Exothermic peak height B (μW/mg)	Exothermic peak B /Endothermic peak A	As proof stress (MPa)	Breaking elongation (%)	185°C AB proof stress (MPa)	ΔBH (MPa)	170°C AB proof stress (MPa)	ΔBH (MPa)
Inventive example	1	1	-	-	40	72	9.4	44.6	4.7	133	29	192	59	162	29
Inventive example	2	1	100	200	40	72	6.9	32.7	4.7	132	27	213	81	192	60
Comparative example	1	1	-	-	-	-	13.3	51.7	3.9	139	30	171	32	168	29
Comparative example	2	1	-	-	40	1	12.6	50.6	4.0	136	28	174	38	172	36
Comparative example	3	1	-	-	80	5	4.2	14.3	3.4	138	24	240	102	210	72
Comparative example	4	1	-	-	50	1000	2.9	16.8	5.8	144	24	245	101	208	64
Comparative example	5	1	200	500	40	72	2.5	12.4	5.0	174	19	293	119	266	92
Comparative example	6	1	-	-	100	5	1.3	25.2	19.4	138	24	243	105	214	76
Inventive example	3	2	-	-	50	72	8.7	42.6	4.9	125	28	203	78	173	48
Inventive example	4	3	-	-	40	300	6.8	46.8	6.9	136	31	217	81	182	46
Inventive example	5	4	-	-	60	8	8.8	43.9	5.0	136	26	213	77	185	49
Inventive example	6	4	250	10	40	6	6.7	31.3	4.7	134	26	226	92	201	67
Inventive example	7	5	150	60	50	8	5.8	28.4	4.9	131	26	220	89	196	65
Inventive example	8	6	200	10	40	72	4.3	30.3	7.0	123	26	198	75	190	67
Comparative example	7	7	-	-	40	72	1.4	15.3	10.9	100	29	146	46	139	39
Comparative example	8	8	-	-	40	72	1.2	12.7	10.6	91	27	138	47	133	42

[0103] Although the present invention was explained in detail referring to the predetermined aspects, it is obvious for a person with an ordinary skill in the art that various alterations and amendments are possible without deviating from the spirit and scope of the present invention.

[0104] The present application is based on the Japanese Patent Application (JP-A No. 2016-067007) applied on March 30, 2016 and the Japanese Patent Application (JP-A No. 2016-213789) applied on October 31, 2016, and the contents of them are hereby incorporated as the reference into the present application.

Industrial Applicability

[0105] According to the present invention, a 6000-series aluminum alloy sheet can be provided which is provided with both of the excellent formability and the high BH property even after the room temperature temper aging for a long time and with the paint-bake hardening treatment at a high temperature. That is, both of the excellent formability even after the room temperature temper aging for a long time and the high BH property even in the conventional paint-bake hardening treatment at a low temperature described above as well as in the paint-bake hardening treatment at a high temperature described above can be provided. As a result, application of the 6000-series aluminum alloy sheet can be expanded as an automotive member including a panel material.

Claims

1. An aluminum alloy sheet excellent in formability and paint-bake hardenability, containing: in terms of mass%, Mg: 0.3-1.5% and Si: 0.6-1.5% respectively, the total of the Mg content and the Si content being greater than 1.2%, the balance including Al and inevitable impurities, wherein, in a differential scanning calorimetric curve of the aluminum alloy sheet, endothermic peaks whose height A is 3-10 μW/mg exist within a temperature range of 150-230°C, exothermic peaks whose height B is 20-50 μW/mg exist within a temperature range of 230°C or above and below 330°C, and a ratio B/A of a maximum peak height B out of the exothermic peaks to a maximum peak height A out of the endothermic peaks is greater than 3.5 and less than 15.0.

2. The aluminum alloy sheet excellent in formability and paint-bake hardenability according to claim 1, wherein
the height A of the endothermic peak is 3-8 μW/mg, and
the height B of the exothermic peak is 20-40 μW/mg.

3. The aluminum alloy sheet excellent in formability and paint-bake hardenability according to claim 1 or 2, wherein
the aluminum alloy sheet further contains one kind or two kinds or more, in terms of mass%, selected from Cu: 0.02-0.8%, Fe: 0.05-0.5%, Mn: 0.05-0.3%, Zr: 0.04-0.1%, Cr: 0.04-0.3%, V: 0.02-0.1%, Ag: 0.01-0.1%, and Zn: 0.01-0.3%.

4. A manufacturing method of an aluminum alloy sheet excellent in formability and paint-bake hardenability, comprising: a step of subjecting an aluminum alloy cold rolled sheet to a preliminary temper aging treatment at a low temperature and for a long time, the aluminum alloy cold rolled sheet containing, in terms of mass%, Mg: 0.3-1.5% and Si: 0.6-1.5% respectively, the total of the Mg content and the Si content being greater than 1.2%, the balance including Al and inevitable impurities, the preliminary temper aging treatment being for holding the aluminum alloy cold rolled sheet for 5 hours or more and 500 hours or less at the temperature range of 30°C-60°C within one hour after a solution heat treatment and quenching treatment, thereby, in a differential scanning calorimetric curve before the aluminum alloy cold rolled sheet is subjected to an artificial temper aging treatment, endothermic peaks whose height A is 3-10 μW/mg are made to exist within a temperature range of 150-230°C, exothermic peaks whose height B is 20-50 μW/mg are made to exist within a temperature range of 230°C or above and below 330°C, and a ratio B/A of the exothermic peak height B to the endothermic peak height A is made to be greater than 3.5 and less than 15.0.

5. The manufacturing method of an aluminum alloy sheet excellent in formability and paint-bake hardenability according to claim 4, wherein
the aluminum alloy sheet further contains one kind or two kinds or more, in terms of mass%, selected from Cu: 0.02-0.8% , Fe: 0.05-0.5%, Mn: 0.05-0.3%, Zr: 0.04-0.1%, Cr: 0.04-0.3%, V: 0.02-0.1%, Ag: 0.01-0.1%, and Zn: 0.01-0.3%.

6. The manufacturing method of an aluminum alloy sheet excellent in formability and paint-bake hardenability according to claim 4 or 5, further comprising the steps of:

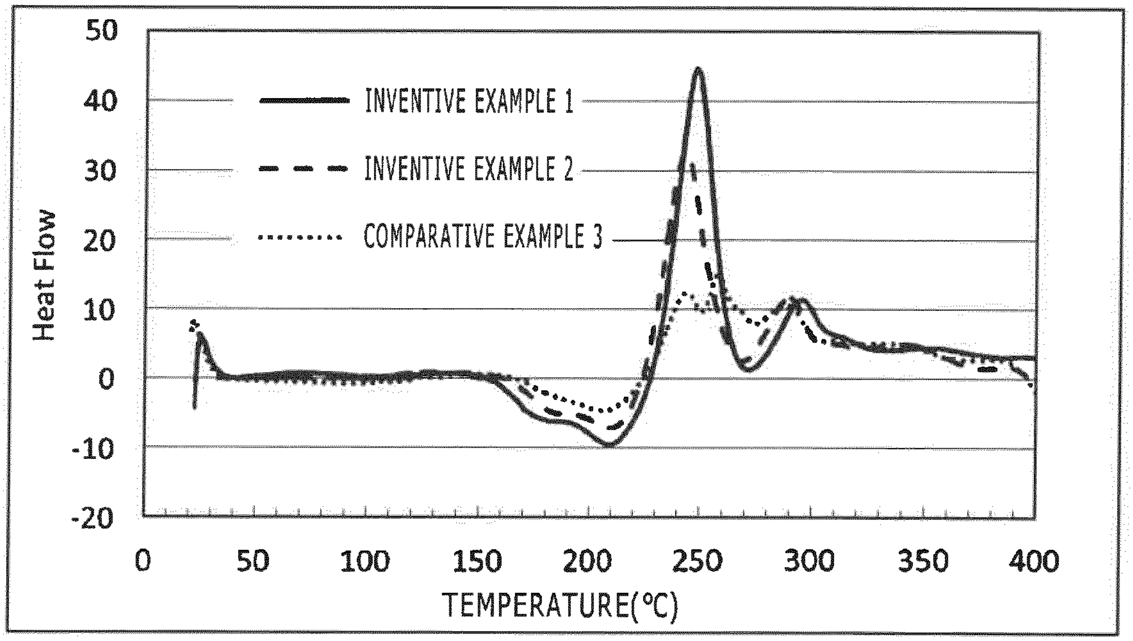
performing a preliminary temper aging treatment at a high temperature and for a short time for holding the aluminum alloy sheet for 5 seconds or more and 300 seconds or less at the temperature range of 100°C-300°C within one hour after the solution heat treatment and quenching treatment; and
thereafter performing up to the preliminary temper aging treatment at a low temperature and for a long time.

7. The manufacturing method of an aluminum alloy sheet excellent in formability and paint-bake hardenability according to claim 4, wherein
the aluminum alloy sheet is painted after being formed, and is subjected to a paint-bake hardening treatment in a condition of the heating temperature of 180-230°C and the heating holding time of 10-30 minutes.

8. The manufacturing method of an aluminum alloy sheet excellent in formability and paint-bake hardenability according to claim 5, wherein
the aluminum alloy sheet is painted after being formed, and is subjected to a paint-bake hardening treatment in a condition of the heating temperature of 180-230°C and the heating holding time of 10-30 minutes.

9. The manufacturing method of an aluminum alloy sheet excellent in formability and paint-bake hardenability according to claim 6, wherein
the aluminum alloy sheet is painted after being formed, and is subjected to a paint-bake hardening treatment in a condition of the heating temperature of 180-230°C and the heating holding time of 10-30 minutes.

FIG.1


INVENTIVE EXAMPLE 1
INVENTIVE EXAMPLE 2
COMPARATIVE EXAMPLE 3
Heat Flow
50
40
30
20
10
0
-10
-20
0
50
100
150
200
250
300
350
400
TEMPERATURE(°C)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/013179

A. CLASSIFICATION OF SUBJECT MATTER

C22C21/02(2006.01)i, *C22C21/06*(2006.01)i, *C22C21/12*(2006.01)i, *C22F1/05* (2006.01)i, *C22F1/00*(2006.01)n

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C21/02, C22C21/06, C22C21/12, C22F1/05, C22F1/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2017
Kokai Jitsuyo Shinan Koho	1971-2017	Toroku Jitsuyo Shinan Koho	1994-2017

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	JP 2003-105471 A (Sumitomo Light Metal Industries, Ltd.), 09 April 2003 (09.04.2003), paragraphs [0014] to [0020], [0025] to [0026]; fig. 2, 6, 7, test material no.32 (Family: none)	1-5 6-9
X A	JP 2016-020530 A (UACJ Corp.), 04 February 2016 (04.02.2016), paragraphs [0054] to [0060]; tables 1 to 3 (Family: none)	1-2,4 7-9
X	JP 2011-017063 A (Furukawa-Sky Aluminum Corp.), 27 January 2011 (27.01.2011), paragraphs [0034] to [0043], [0072] to [0087]; tables 1 to 3, condition code 7 (Family: none)	1-2,4

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance
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"&" document member of the same patent family

Date of the actual completion of the international search 22 May 2017 (22.05.17)	Date of mailing of the international search report 30 May 2017 (30.05.17)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/013179

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2012-041567 A (Sumitomo Light Metal Industries, Ltd.), 01 March 2012 (01.03.2012), (Family: none)	6-9
A	JP 2013-167004 A (Kobe Steel, Ltd.), 29 August 2013 (29.08.2013), & US 2015/0007909 A1	1-9

Form PCT/ISA/210 (continuation of second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 4117243 B **[0013]**
- JP 2013167004 A **[0013]**
- JP 2015196852 A **[0013]**
- JP 2015196853 A **[0013]**
- JP 3819263 B **[0013]**
- JP 2016067007 A **[0104]**
- JP 2016213789 A **[0104]**