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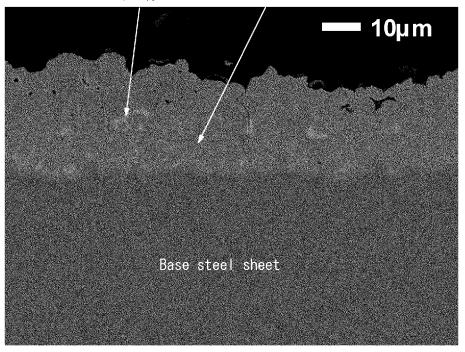
# (54) HOT-PRESSED MEMBER, METHOD FOR MANUFACTURING SAME, AND PLATED STEEL SHEET FOR HOT PRESSING

(57) Disclosed is a hot pressed member that has excellent painting layer adhesion and post-painting corrosion resistance when subjected to electrodeposition painting after zirconium-based chemical conversion treatment. A hot pressed member disclosed herein includes: a base steel sheet; a Fe-Zn-Al-Mg-based alloy coated layer containing an  $\alpha$ -Fe phase and a  $\Gamma$  phase and formed on at least one surface of the base steel sheet at a coating weight per surface of 40-400 g/m²; and an oxide layer containing Zn, Al, and Mg and formed on the

Fe-Zn-Al-Mg-based alloy coated layer, in which a ratio of  $I_{\Gamma}/I_{\alpha}$  is 0.5 or less when measured by X-ray diffraction using a Co-K $\alpha$  (wavelength: 1.79021 Å) radiation source at an incident angle of 25°, where Ir is an intensity of a diffraction peak of (411) plane of the  $\Gamma$  phase present in an angular range of 41.5°≤20≤43.0° and  $I_{\alpha}$  is an intensity of a diffraction peak of (110) plane of the  $\alpha$ -Fe phase present in an angular range of 51.0°≤20≤52.0°, and a sum of Al and Mg concentrations in the oxide layer is 28 atomic% or more.

FIG. 1

 $\Gamma\operatorname{-Fe}_3\operatorname{Zn}_{10}$  phase Solute ( $\alpha\operatorname{-Fe}$ ) phase



#### Description

**TECHNICAL FIELD** 

<sup>5</sup> [0001] This disclosure relates to a hot pressed member and a method of producing the same, and a coated steel sheet for hot press forming.

**BACKGROUND** 

[0002] Conventionally, most automotive undercarriage parts and automotive body structural parts are produced by press working steel sheets with certain strength. In recent years, there has been an eagerness to reduce the weight of automobile automotive body from the perspective of preserving the global environment, and efforts have been made to increase the strength of the steel sheets used and to reduce their thickness. However, when a steel sheet has higher strength, its press formability is deteriorated, and forming the steel sheet into the desired part shape is becoming more difficult.

**[0003]** To address these issues, a working technique called hot press forming has been proposed. Hot press forming uses a press mold having a die and a punch to process a heated steel sheet while quenching it simultaneously, to achieve both easier working and higher strength. Among others, Zn alloy-coated steel sheets have attracted attention as steel sheets for hot press forming having high rust resistance since their coated layers, which are electrochemically more basic (with a lower potential) than the base steel sheets, remain after heating. Accordingly, hot pressed members using such Zn alloy-coated steel sheets and manufacturing methods thereof have been proposed in the art.

**[0004]** JP 2006-265706 A (PTL 1) describes a coated steel sheet for hot press forming having a coated layer in which an Al concentration {Al} is in the range of 0.2 g/m² to 1.0 g/m² and a Mg concentration {Mg} in mass % satisfies a relation with the Al concentration of  $0.10 \le \{Mg\}/\{Al\} \le 5$ , and a hot pressed member obtained by heating the coated steel sheet for hot press forming and then subjecting it to hot press forming.

CITATION LIST

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Patent Literature

[0005] [PTL 1] JP 2006-265706 A

**SUMMARY** 

35 (Technical Problem)

[0006] PTL 1 describes that the hot pressed member has good post-painting corrosion resistance when subjected to electrodeposition painting (also called electrodeposition coating) after zinc phosphate-based chemical conversion treatment. In recent years, zirconium-based chemical conversion treatment has begun to replace the conventional zinc phosphate-based chemical conversion treatment. As such, hot pressed members are also increasingly required to have proper painting layer adhesion and post-painting corrosion resistance when subjected to electrodeposition painting after zirconium-based chemical conversion treatment. However, our examination revealed that although the hot pressed member described in PTL 1 has good post-painting corrosion resistance when subjected to electrodeposition painting after zinc phosphate-based chemical conversion treatment, it has insufficient painting layer adhesion and post-painting corrosion resistance when subjected to electrodeposition painting after zirconium-based chemical conversion treatment.

[0007] It would thus be helpful to provide a hot pressed member with excellent painting layer adhesion and post-painting corrosion resistance when subjected to electrodeposition painting after zirconium-based chemical conversion treatment, and a suitable method of producing the same.

**[0008]** It would also be helpful to provide a coated steel sheet for hot press forming that is suitably used as a material to obtain such hot pressed member.

(Solution to Problem)

**[0009]** In order to address the above issues, the present inventors conducted a diligent study and made the following findings.

**[0010]** It is possible to improve the painting layer adhesion and post-painting corrosion resistance of a hot pressed member when subjected to electrodeposition painting after zirconium-based chemical conversion treatment, by restricting precipitation of a  $\Gamma$  phase, which is formed from an electrochemically basic intermetallic compound such as an Fe3Zn10

phase, in an Fe-Zn-Al-Mg-based alloy coated layer of the hot pressed member, and by increasing the total concentration of Al and Mg in a Zn-Al-Mg-containing oxide layer formed on the coated layer.

**[0011]** To produce such a hot pressed member having an Fe-Zn-Al-Mg-based alloy coated layer with a small amount of  $\Gamma$ -phase precipitation and an oxide layer with a large sum of Al and Mg concentrations, it is necessary to heat a coated steel sheet for hot press forming having a Zn-Al-Mg-based alloy coated layer with certain amounts of Al and Mg and a liquidus temperature of 400 °C or lower to a relatively low temperature before subjecting it to hot press forming.

[0012] Based on these discoveries, we provide the following.

- [1] A hot pressed member comprising: a base steel sheet; a Fe-Zn-Al-Mg-based alloy coated layer containing an  $\alpha$ -Fe phase and a  $\Gamma$  phase and formed on at least one surface of the base steel sheet at a coating weight per surface of 40 g/m² to 400 g/m²; and an oxide layer containing Zn, Al, and Mg and formed on the Fe-Zn-Al-Mg-based alloy coated layer, wherein a ratio of  $I_{\Gamma}/I_{\alpha}$  is 0.5 or less when measured by X-ray diffraction using a Co-K $\alpha$  (wavelength: 1.79021 Å) radiation source at an incident angle of 25°, where  $I_{\Gamma}$  is an intensity of a diffraction peak of (411) plane of the  $\Gamma$  phase present in an angular range of 41.5°  $\leq$  20  $\leq$  43.0° and  $I_{\alpha}$  is an intensity of a diffraction peak of (110) plane of the  $\alpha$ -Fe phase present in an angular range of 51.0°  $\leq$  20  $\leq$  52.0°, and a sum of Al and Mg concentrations in the oxide layer is 28 atomic% or more.
- [2] A method of producing a hot pressed member, the method comprising: heating a coated steel sheet for hot press forming to a temperature range of  $Ac_3$  transformation point to  $1000\,^{\circ}$ C, the coated steel sheet for hot press forming comprising: a base steel sheet; and a Zn-Al-Mg-based alloy coated layer formed on at least one surface of the base steel sheet at a coating weight per surface of  $30\,$  g/m² to  $180\,$  g/m², having a chemical composition containing (consisting of), in mass%, Al: 3% to 10% and Mg: 0.2% to 0.8%, with the balance being Zn and inevitable impurities, and having a liquidus temperature in an air atmosphere of  $400\,^{\circ}$ C or lower, and then subjecting the coated steel sheet to hot press forming.
- [3] The method of producing a hot pressed member according to [2], wherein the chemical composition of the Zn-Al-Mg-based alloy coated layer further contains at least one selected from the group consisting of Ca, Sr, Mn, V, Cr, Mo, Ti, Ni, Co, Sb, Zr, and B in a total amount of 1 mass% or less.
- [4] A coated steel sheet for hot press forming comprising: a base steel sheet; and a Zn-Al-Mg-based alloy coated layer formed on at least one surface of the base steel sheet at a coating weight per surface of 30 g/m² to 180 g/m², having a chemical composition containing (consisting of), in mass%, Al: 3 % to 10 % and Mg: 0.2 % to 0.8 %, with the balance being Zn and inevitable impurities, and having a liquidus temperature in an air atmosphere of 400 °C or lower.
- [5] The coated steel sheet for hot press forming according to [4], wherein the chemical composition of the Zn-Al-Mg-based alloy coated layer further contains at least one selected from the group consisting of Ca, Sr, Mn, V, Cr, Mo, Ti, Ni, Co, Sb, Zr, and B in a total amount of 1 mass% or less.

(Advantageous Effect)

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**[0013]** The hot pressed member according to the present disclosure has excellent painting layer adhesion and post-painting corrosion resistance when subjected to electrodeposition painting after zirconium-based chemical conversion treatment. In addition, the method of producing a hot pressed member according to the present disclosure enables the production of a hot pressed member with excellent painting layer adhesion and post-painting corrosion resistance when subjected to electrodeposition painting after zirconium-based chemical conversion treatment.

**[0014]** The coated steel sheet for hot press forming according to the present disclosure is suitably used as a raw material for producing a hot pressed member with excellent painting layer adhesion and post-painting corrosion resistance when subjected to electrodeposition painting after zirconium-based chemical conversion treatment.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0015] In the accompanying drawings:

FIG. 1 is a scanning electron microscope (SEM) micrograph of a cross-section of an Fe-Zn-Al-Mg-based alloy coated layer of a hot pressed member in No. 2 representing one of our examples; and

FIG. 2 is an SEM micrograph of a cross-section of an Fe-Zn-Al-Mg-based alloy coated layer of a hot pressed member in No. 8 representing one of comparative examples.

#### DETAILED DESCRIPTION

(Hot Pressed Member)

**[0016]** A hot pressed member according to one of the embodiments disclosed herein comprises: a base steel sheet; an Fe-Zn-Al-Mg-based alloy coated layer formed on at least one surface of the base steel sheet; and an oxide layer formed on the Fe-Zn-Al-Mg-based alloy coated layer.

[Base Steel Sheet]

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**[0017]** Although the base steel sheet of the hot pressed member in this embodiment is not limited to a particular steel sheet, it is preferable to use a steel sheet having the chemical composition as described in the section "(Coated Steel Sheet for Hot Press Forming)" below, in order for the resulting hot pressed member to have a tensile strength TS of 1470 MPa or more.

[Fe-Zn-Al-Mg-based Alloy Coated Layer]

**[0018]** The Fe-Zn-Al-Mg-based alloy coated layer in the hot pressed member in this embodiment contains, preferably consists of, an  $\alpha$ -Fe phase and a  $\Gamma$  phase.

[0019] The  $\alpha$ -Fe phase is a solid solution phase that is mainly composed of Fe and contains Zn, Al, and Mg. When a coated steel sheet for hot press forming with a Zn-Al-Mg-based alloy coated layer is subjected to hot press forming, Zn, Al, and Mg in the coated layer diffuse into the base steel sheet and, in this diffusion region, a solid solution phase ( $\alpha$ -Fe phase) mainly composed of Fe and containing Zn, Al, and Mg is formed. The  $\alpha$ -Fe phase is formed so as to erode the surface layer of the base steel sheet of the coated steel sheet. However, in a hot pressed member, the  $\alpha$ -Fe phase is generally interpreted to be part of the Fe-Zn-Al-Mg-based alloy coated layer located on the base steel sheet.

[0020] The  $\Gamma$  phase is a phase formed from an intermetallic compound that is mainly composed of Zn and contains Al, Mg, and Fe. Primarily, the  $\Gamma$  phase is composed of Fe3Zn10 phase. In this respect,  $\Gamma$ 1 phase has a crystal structure similar to that of  $\Gamma$  phase and is difficult to distinguish by X-ray diffraction. Thus, as used herein, " $\Gamma$  phase" is intended to include  $\Gamma$ 1 phase. Other compositional intermetallic compounds that make up the  $\Gamma$  phase include, for example, Fe4Zn9, FeZn4, and Fe5Zn21. During hot press forming, the Zn-Al-Mg-based alloy coated layer that remains without contributing to diffusion into the base steel sheet incorporates Fe diffused from the base steel sheet, forming a  $\Gamma$  phase composed of an intermetallic compound and forming a part of the Fe-Zn-Al-Mg-based alloy coated layer in the hot pressed member.

**[0021]** The  $\alpha$ -Fe and  $\Gamma$  phases can be distinguished from each other by their distinctly different contrasts in the cross-sectional SEM images of the Fe-Zn-Al-Mg-based alloy coated layer of the hot pressed member. Referring to FIGS. 1 and 2, regions that appear relatively bright in the surface layer of the hot pressed member are the  $\Gamma$  phase, and regions that appear relatively dark are the  $\alpha$ -Fe phase. The  $\alpha$ -Fe and  $\Gamma$  phases can also be identified using a Co-K $\alpha$  (wavelength: 1.79021 Å) radiation source at an incident angle of 25°.

**[0022]** The  $\Gamma$  phase in the Fe-Zn-Al-Mg-based alloy coated layer has a significantly lower potential than the base steel sheet and the  $\alpha$ -Fe phase, and is therefore preferentially corroded when exposed to a corrosion environment. In other words, the  $\Gamma$  phase provides sacrificial protection against the base steel sheet and the  $\alpha$ -Fe phase.

[0023] A zinc phosphate-based chemical conversion treatment layer functions as an excellent corrosion inhibitor against Zn-based alloys. Therefore, when a hot pressed member obtained by subjecting a Zn-Al-Mg-based alloy-coated steel sheet to hot press forming is subjected to electrodeposition painting after zinc phosphate-based chemical conversion treatment, the resulting member has a low corrosion rate in the  $\Gamma$  phase and a sufficiently low corrosion rate under the painting layer such that post-painting corrosion resistance is not an issue in actual use environments even in a sacrificial protection state due to flaws that penetrate the painting layer, the chemical conversion treatment layer, and the coated layer to reach the base steel sheet.

[0024] In contrast, a zirconium oxide-based chemical conversion treatment layer does not have a corrosion inhibitor function against Zn-based alloys. Therefore, in a sacrificial protection state, the corrosion rate of the  $\Gamma$  phase becomes higher, resulting in a higher corrosion rate under the painting layer. Then, if a large amount of  $\Gamma$  phase is present contiguously in the Fe-Zn-Al-Mg-based alloy coated layer, corrosion in the  $\Gamma$  phase propagates in-plane under the painting layer in a sacrificial protection state, resulting in problems in lowered esthetics such as poor appearance including swelling in the painting layer. Therefore, when applying a zirconium-based chemical conversion treatment, it is important to limit the amount of  $\Gamma$  phase to ensure post-painting corrosion resistance.

**[0025]** Therefore, in this embodiment, as one of the necessary conditions to improve the post-painting corrosion resistance when the hot pressed member is subjected to electrodeposition painting after zirconium-based chemical conversion treatment, it is important to suppress the precipitation of a  $\Gamma$  phase, which is formed from an electrochemically

basic intermetallic compound such as an Fe3Zn10 phase. Specifically, it is important that a ratio of  $I_{\Gamma}/I_{\alpha}$  is 0.5 or less when measured by X-ray diffraction using a Co-K $\alpha$  (wavelength: 1.79021 Å) radiation source at an incident angle of 25°, where  $I_{\Gamma}$  is an intensity of a diffraction peak of (411) plane of the  $\Gamma$  phase present in an angular range of 41.5°  $\leq$  20  $\leq$  43.0° and  $I_{\alpha}$  is an intensity of a diffraction peak of (110) plane of the  $\alpha$ -Fe phase present in an angular range of 51.0°  $\leq$  20  $\leq$  52.0°. If  $I_{\Gamma}/I_{\alpha}$  is greater than 0.5, the post-painting corrosion resistance is insufficient when the hot pressed member is subjected to electrodeposition painting after zirconium-based chemical conversion treatment. If  $I_{\Gamma}/I_{\alpha}$  is 0.5 or less, the  $\Gamma$  phase is sufficiently broken up by the  $\alpha$ -Fe phase in the Fe-Zn-Al-Mg-based alloy layer, and excellent post-painting corrosion resistance can be obtained when the hot pressed member is subjected to electrodeposition painting after zirconium chemical conversion treatment.

**[0026]** Since a smaller value of  $I_{\Gamma}/I_{\alpha}$  is preferable, the lower limit is not limited. However, the value of  $I_{\Gamma}/I_{\alpha}$  that is detected by measurement using X-ray diffraction as described above is usually 0.01 or more.

**[0027]** The measurement conditions for X-ray diffraction other than the incident angle and radiation source described above, which do not affect the ratio of  $I_{\Gamma}/I_{\alpha}$ , can be adopted as described in the EXAMPLES section below.

Coating Weight Per Surface: 40 g/m<sup>2</sup> to 400 g/m<sup>2</sup>

[0028] By setting the coating weight of the Fe-Zn-Al-Mg-based alloy coated layer of the hot pressed member to 40 g/m² to 400 g/m², it is possible to provide the hot pressed member with excellent corrosion resistance. If the coating weight is less than 40 g/m², it is not possible to provide the hot pressed member with the desired corrosion resistance. If the coating weight exceeds 400 g/m², the number of cracks crossing the coated layer becomes significantly larger due to the solidification and shrinkage of the coated layer after hot pressing, and the adhesion in the coated layer is greatly degraded. The coating weight of the coated layer of the hot pressed member is preferably 50 g/m² or more, and more preferably 60 g/m² or more. The coating weight of the coated layer of the hot pressed member is preferably 350 g/m² or less, and more preferably 300 g/m² or less.

**[0029]** As used herein, the "coating weight per surface of the Fe-Zn-Al-Mg-based alloy coated layer" of the hot pressed member is determined as follows. From each hot pressed member to be evaluated, three 48 mmφ samples are taken by punching. Then, in each sample, a non-evaluated surface opposite the one surface where the coating weight is evaluated is masked. First, the oxide layer is dissolved by immersing each sample in a 20 % chromium oxide (VI) solution at room temperature for 10 minutes. Then, each sample is weighed. Next, 500 mL of a 35 % hydrochloric acid solution to which 3.5 g of hexamethylenetetetramine has been added is mixed up to 1 L. Then, each sample is immersed in the resultant solution for 120 minutes to dissolve the Fe-Zn-Al-Mg-based alloy coated layer. Then, each sample is weighed again. The coating weight per unit area in each sample is calculated from the mass difference before and after the dissolution of the Fe-Zn-Al-Mg-based alloy coated layer. The average of the three samples is then used as the coating weight per surface.

[Oxide Layer]

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**[0030]** The oxide layer of the hot pressed member in this embodiment is formed on the Fe-Zn-Al-Mg-based alloy coated layer and contains Zn, Al, and Mg. When a coated steel sheet for hot press forming with a Zn-Al-Mg-based alloy coated layer is subjected to hot press forming, Zn, Al, and Mg in the coated layer combine with oxygen present in the heating atmosphere to form an oxide layer containing Zn, Al, and Mg. The oxide layer is mainly composed of an Al oxide. However, it may also contain Zn and Mg contained in the coated layer, as well as elements constituting the base steel sheet, such as Fe, Mn, and Cr.

[0031] In this embodiment, as another necessary condition for improving the post-painting corrosion resistance when the hot pressed member is subjected to electrodeposition painting after zirconium-based chemical conversion treatment, it is important that the sum of the AI and Mg concentrations in the oxide layer be 28 atomic% or more. If the sum of the AI and Mg concentrations in the oxide layer is less than 28 atomic%, even with the ratio of  $I_{\Gamma}/I_{\alpha}$  being 0.5 or less, the post-painting corrosion resistance is insufficient when the hot pressed member is subjected to electrodeposition painting after zirconium-based chemical conversion treatment. This is presumably because when the concentration of Zn constituting the oxide layer is high, the reaction between the chemical conversion treatment liquid and the oxide layer becomes non-uniform, resulting in a larger unevenness in the thickness of the zirconium-based chemical conversion treatment layer formed on the surface of the oxide layer. In other words, it is assumed that regions where the chemical conversion treatment layer becomes thin are formed more easily, resulting in reduced adhesion either between the oxide layer and the chemical conversion treatment layer and the painting layer, or incomplete coverage by the chemical conversion treatment layer. In contrast, if the sum of the AI and Mg concentrations in the oxide layer is 28 atomic% or more, a zirconium-based chemical conversion treatment layer is appropriately formed, and the hot pressed member may have excellent post-painting corrosion resistance when subjected to electrodeposition painting after zirconium-based chemical conversion treatment.

**[0032]** If the sum of the AI and Mg concentrations in the oxide layer is less than 28 atomic%, the oxide layer becomes brittle, resulting in insufficient painting layer adhesion when the hot pressed member is subjected to electrodeposition painting after the zirconium-based chemical conversion treatment. In contrast, if the sum of the AI and Mg concentrations in the oxide layer is 28 atomic% or more, the oxide layer has sufficient strength, and the hot pressed member has good painting layer adhesion when subjected to electrodeposition painting after zirconium-based chemical conversion treatment.

**[0033]** The upper limit of the sum of the Al and Mg concentrations in the oxide layer is not particularly limited. However, an oxide layer containing excessively high concentrations of Al and Mg is chemically stable in acidic environments, such as in a chemical conversion treatment liquid for coating base treatment, and may prevent the formation of a chemical conversion treatment layer. Therefore, the sum of the Al and Mg concentrations in the oxide layer is preferably 50 atomic% or less.

[0034] In this embodiment, the oxide layer is formed very thinly on the Fe-Zn-Al-Mg-based alloy coated layer, and thus may not be visible in the cross-sectional SEM image as illustrated in FIG. 1. However, by cross-sectioning the surface layer of the hot pressed member using energy dispersive X-ray analysis (EDX) combined with SEM, elemental mapping can be performed to identify the oxide layer as a region where oxygen is detected. As used herein, "the Al and Mg concentrations in the oxide layer" are the values measured by the following methods. Specifically, a test specimen for cross-sectional observation is taken from a flat part of the hot pressed member. A cross-section of the test specimen including the Fe-Zn-Al-Mg-based alloy coated layer and the oxide layer is observed under SEM at 10000× magnification and accelerating voltage of 15 kV, and the composition of the oxide layer is measured at freely-selected three locations using EDX. The arithmetic means of the Al concentrations and Mg concentrations at the three locations are respectively used as the "Al concentration in the oxide layer" and "Mg concentration in the oxide layer".

(Method of Producing the Hot Pressed Member)

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**[0035]** A method of producing the hot pressed member according to one of the embodiments of the present disclosure comprises: heating a coated steel sheet for hot press forming according to one of the embodiments of the present disclosure as described below to a temperature range of Ac<sub>3</sub> transformation point to 1000 °C; and then subjecting the coated steel sheet to hot press forming.

[0036] By setting the heating temperature of the steel sheet for hot press forming before hot press forming to the temperature range of  $Ac_3$  transformation point to 1000~C, it is possible to obtain an Fe-Zn-Al-Mg-based alloy coated layer with  $\alpha$ -Fe and  $\Gamma$  phases as well as an oxide layer with predetermined Al and Mg concentrations, as described above. When the heating temperature is lower than the  $Ac_3$  transformation point, the  $I_{\Gamma}/I_{\alpha}$  of the Fe-Zn-Al-Mg-based alloy coated layer exceeds 0.5 after hot press forming. Consequently, the post-painting corrosion resistance becomes insufficient when the hot pressed member is subjected to electrodeposition painting after zirconium-based chemical conversion treatment. If the heating temperature exceeds 1000~C, the desired oxide layer cannot be obtained, and the painting layer adhesion and post coating corrosion resistance are insufficient when the hot pressed member is subjected to electrodeposition painting after zirconium-based chemical conversion treatment. As used herein, the "heating temperature" refers to the maximum arrival temperature of the steel sheet. As used herein, "  $Ac_3$  transformation point" is a value calculated from the following formula based on the chemical composition of the steel sheet:

Ac<sub>3</sub> transformation point (°C) =  $910 - 203C^{1/2} + 44.7Si - 4Mn + 11Cr$ .

The element symbols on the right side of the formula indicate the content of each element. When Cr is not contained, Cr = 0. **[0037]** Although there is no limitation on the holding time after the temperature is raised to the heating temperature, the holding time is desirably 30 seconds or longer from the viewpoint of eliminating the  $\Gamma$  phase and avoiding liquid metal embrittlement cracking during hot press forming. From the perspective of avoiding hydrogen ingress due to the inclusion of water vapor present in the furnace during the holding time, the holding time is preferably within 5 minutes, more preferably within 3 minutes, and even more preferably within 2 minutes.

**[0038]** The method of heating the steel sheet for hot press forming is not limited in any way, and exemplary methods include furnace heating such as heating in an electric or gas furnace, electrical resistance heating, induction heating, high-frequency heating, and flame heating.

**[0039]** In hot press forming, the coated steel sheet for hot press forming heated as described above is simultaneously subjected to press forming and quenching using a press forming tool to obtain a hot pressed member of a predetermined shape. The conditions for hot press forming are not limited, and conventional methods may be followed.

(Coated Steel Sheet for Hot Press Forming)

**[0040]** The coated steel sheet for hot press forming according to one of the embodiments of the present disclosure comprises: a base steel sheet; and a Zn-Al-Mg-based alloy coated layer formed on at least one surface of the base steel sheet at a coating weight per surface of 30 g/m² to 180 g/m², having a chemical composition containing, in mass%, Al: 3 % to 10 % and Mg: 0.2 % to 0.8 %, with the balance being Zn and inevitable impurities, and having a liquidus temperature in an air atmosphere of 400 °C or lower.

[Base Steel Sheet]

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**[0041]** To obtain a hot pressed member having a tensile strength TS of 1470 MPa or more, for example, it is preferable that the base steel sheet have a chemical composition containing, in mass%, C: 0.20 % to 0.35 %, Si: 0.1 % to 0.5 %, Mn: 1.0 % to 3.0 %, P: 0.1 % or less, S: 0.05 % or less, Al: 0.1 % or less, N: 0.01 % or less, with the balance being Fe and inevitable impurities. The base steel sheet may be a cold-rolled steel sheet or a hot-rolled steel sheet. The reasons for the limitation of each component will be explained below.

C: 0.20 % to 0.35 %

[0042] C increases strength by forming a steel microstructure such as martensite. To obtain a TS of 1470 MPa or more, the C content needs to be 0.20 % or more. However, if the C content exceeds 0.35 %, the toughness deteriorates at a spot welded portion. Therefore, the C content is preferably 0.20 % to 0.35 %.

Si: 0.1 % to 0.5 %

[0043] Si is an effective element in increasing the strength of steel to obtain good material properties. To this end, the Si content needs to be 0.1 % or more. However, if the Si content exceeds 0.5 %, ferrite is stabilized and hardenability is reduced. Therefore, the Si content is preferably 0.1 % to 0.5 %.

Mn: 1.0 % to 3.0 %

**[0044]** Mn is an effective element for increasing the strength of steel. To ensure proper mechanical properties and strength, the Mn content needs to be 1.0 % or more. However, if the Mn content exceeds 3.0 %, surface enrichment during annealing becomes more pronounced, making it difficult to ensure proper coating adhesion. Therefore, the Mn content is preferably 1.0 % to 3.0 %.

P: 0.1 % or less

**[0045]** If the P content exceeds 0.1 %, the balance between strength and ductility is reduced as a result of degradation in local ductility due to grain boundary embrittlement caused by P segregation at austenite grain boundaries during casting. Therefore, the P content is preferably 0.1 % or less. From the viewpoint of steelmaking cost, the P content is preferably 0.01 % or more.

S: 0.05 % or less

45 [0046] S forms as inclusions such as MnS, which cause degradation of impact resistance and cracking along the metal flow in welded portions. Therefore, a lower S content is desirable, and the S content is preferably 0.05 % or less. To ensure good stretch flangeability, the S content is more preferably 0.01 % or less. From the viewpoint of steelmaking cost, the S content is preferably 0.002 % or more.

50 Al: 0.1 % or less

**[0047]** If the Al content exceeds 0.1 %, the blanking workability and hardenability of the base steel sheet decrease. Therefore, the Al content is preferably 0.1 % or less. From the viewpoint of ensuring its effectiveness as a deoxidizing material, the Al content is preferably 0.01 % or more.

N: 0.01 % or less

[0048] If the N content exceeds 0.01 %, AIN is formed during hot rolling or heating before hot press forming, and the

blanking workability and hardenability of the base steel sheet decrease. Therefore, the N content is preferably 0.01 % or less. From the viewpoint of steelmaking cost, the N content is preferably 0.001 % or more.

**[0049]** The balance other than the above elements is Fe and inevitable impurities. However, the chemical composition may optionally contain at least one selected from the group consisting of Nb: 0.05 % or less, Ti: 0.05 % or less, B: 0.0002 % to 0.005 %, Cr: 0.1 % to 0.3 %, Sb: 0.003 % to 0.03 %, for the reasons given below.

Nb: 0.05 % or less

[0050] Nb is an effective component for increasing the strength of steel. However, excessive addition of Nb reduces shape fixability. Therefore, when Nb is contained, the Nb content is 0.05 % or less.

Ti: 0.05 % or less

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**[0051]** As in Nb, Ti is also effective in increasing the strength of steel. However, excessive addition of Ti reduces shape fixability. Therefore, when Ti is contained, the Ti content is 0.05 % or less.

B: 0.0002 % to 0.005 %

[0052] B has an effect of inhibiting the formation and growth of ferrite from austenite grain boundaries. Therefore, the B content is preferably 0.0002 % or more. However, excessive addition of B greatly impairs formability. Therefore, when B is contained, the B content is 0.005 % or less.

Cr: 0.1 % to 0.3 %

[0053] Cr is useful for increasing the strength and hardenability of steel. To obtain this effect, the Cr content is preferably 0.1 % or more. However, from the viewpoint of alloy cost, when Cr is contained, the Cr content is 0.3 % or less.

Sb: 0.003 % to 0.03 %

[0054] Sb has an effect of deterring decarburization of the surface layer of the steel sheet during hot pressing. To obtain this effect, the Sb content is preferably 0.003 % or more. However, if the Sb content exceeds 0.03 %, the rolling load increases, resulting in lower productivity. Therefore, when Sb is contained, the Sb content is 0.03 % or less.

[Zn-Al-Mg-based Alloy Coated Layer]

**[0055]** In this embodiment, the Zn-Al-Mg-based alloy coated layer of the coated steel sheet for hot press forming has a chemical composition containing, in mass%, Al: 3 % to 10 % and Mg: 0.2 % to 0.8 %, with the balance being Zn and inevitable impurities, and has a liquidus temperature in an air atmosphere of 400 °C or lower.

40 Al: 3 % to 10 %

[0056] If the AI content is less than 3 %, the  $I_{\Gamma}/I_{\alpha}$  of the Fe-Zn-AI-Mg-based alloy coated layer exceeds 0.5 after hot press forming, and the sum of the AI and Mg concentrations in the oxide layer is less than 28 atomic%. As a result, the painting layer adhesion and post-painting corrosion resistance are insufficient when the hot pressed member is subjected to electrodeposition painting after zirconium-based chemical conversion treatment. If the AI content is less than 3 %, depending on the Mg content, the liquidus temperature to be described later cannot be lowered to 400 °C or lower. On the other hand, if the AI content exceeds 10 %, the liquidus temperature to be described later cannot be lowered to 400 °C or lower, with the result that the  $I_{\Gamma}/I_{\alpha}$  of the Fe-Zn-AI-Mg-based alloy coated layer exceeds 0.5 after hot press forming. Consequently, the post-painting corrosion resistance becomes insufficient when the hot pressed member is subjected to electrodeposition painting after zirconium-based chemical conversion treatment. Therefore, the AI content is 3 % to 10 %.

Mg: 0.2 % to 0.8 %

[0057] When the Mg content is less than 0.2 %, the  $I_{\Gamma}/I_{\alpha}$  of the Fe-Zn-Al-Mg-based alloy coated layer exceeds 0.5 after hot press forming. Consequently, the post-painting corrosion resistance becomes insufficient when the hot pressed member is subjected to electrodeposition painting after zirconium-based chemical conversion treatment. Therefore, the Mg content is 0.2 % or more, preferably 0.3 % or more, and more preferably 0.4 % or more. However, if the Mg content

exceeds 0.8 %, the sum of the AI and Mg concentrations in the oxide layer is less than 28 atomic% after hot press forming. Consequently, the painting layer adhesion and post-painting corrosion resistance becomes insufficient when the hot pressed member is subjected to electrodeposition painting after zirconium-based chemical conversion treatment. Therefore, the Mg content is 0.8 % or less, preferably 0.7 % or less, and more preferably 0.6 % or less.

Liquidus Temperature in Air Atmosphere: 400 °C or lower

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**[0058]** In this embodiment, it is important to keep the liquidus temperature of the Zn-Al-Mg-based alloy coated layer in an air atmosphere at or below 400°C by controlling the Al and Mg contents as appropriate. If the liquidus temperature is above 400 °C, the  $I_{\Gamma}/I_{\alpha}$  of the Fe-Zn-Al-Mg-based alloy coated layer exceeds 0.5 after hot press forming. Consequently, the post-painting corrosion resistance becomes insufficient when the hot pressed member is subjected to electrodeposition painting after zirconium-based chemical conversion treatment. The lower limit of the liquidus temperature is not particularly limited, yet in the range of Al and Mg contents specified above, the liquidus temperature is generally 380 °C or higher. The liquidus temperatures of the Zn-Al-Mg-based alloy coated layer in an air atmosphere are calculated by Thermo Calc, a thermodynamic calculation software, using a database.

[0059] The inevitable impurities contained in the Zn-Al-Mg-based alloy coated layer include components of the base steel sheet that are incorporated into the coated layer by the reaction between the coating bath and the base steel sheet during the coating treatment, inevitable impurities in the coating bath, and so on. The components of the base steel sheet that are incorporated into the coated layer include Fe in an amount of 0.01 % to several percent. The inevitable impurities in the coating bath include, for example, Fe, Cr, Cu, Mo, Ni, and Zr. As to Fe in the coated layer, it is not possible to quantify the amount of Fe incorporated from the base steel sheet and the amount of Fe incorporated from the coating bath separately. Although the total content of inevitable impurities is not limited, from the viewpoint of uniform melting of the coated layer during the process of hot press forming, the total amount of inevitable impurities, excluding Fe, is preferably 1 mass% or less.

**[0060]** The chemical composition of the Zn-Al-Mg-based alloy coated layer may further contain at least one selected from the group consisting of Ca, Sr, Mn, V, Cr, Mo, Ti, Ni, Co, Sb, Zr, and B in a total amount of 1 mass% or less.

Coating Weight Per Surface: 30 g/m<sup>2</sup> to 180 g/m<sup>2</sup>

**[0061]** By setting the coating weight of the Zn-Al-Mg-based alloy coated layer in the range of 30 g/m² to 180 g/m², it is possible to obtain a hot pressed member that is excellent in corrosion resistance and resistance to liquid metal embrittlement cracking during hot press forming. If the coating weight is less than 30 g/m², it is not possible to obtain a hot pressed member with the desired corrosion resistance. If the coating weight exceeds 180 g/m², alloying is not completed in the heating process before hot press forming, and the liquid phase remains. This may cause liquid metal embrittlement cracking. The coating weight of the Zn-Al-Mg-based alloy coated layer is preferably 45 g/m² or more, and more preferably 55 g/m² or more. The coating weight of the Zn-Al-Mg-based alloy coated layer is preferably 120 g/m² or less, and more preferably 100 g/m² or less.

[0062] As used herein, the "coating weight per surface of the Zn-Al-Mg-based alloy coated layer" is determined as follows. From each of the Zn-Al-Mg alloy-coated steel sheets to be evaluated, three 48 mmφ samples are taken by punching. Then, each sample is weighed. Subsequently, in each sample, a non-evaluated surface opposite the one surface where the coating weight is evaluated is masked. Then, 500 mL of a 35 % hydrochloric acid solution to which 3.5 g of hexamethylenetetetramine has been added is mixed up to 1 L. Then, each sample is immersed in the resultant solution for 10 minutes to dissolve the Zn-Al-Mg-based alloy coated layer. Then, each sample is weighed again. The coating weight per unit area in each sample is calculated from the mass difference before and after the dissolution of the Zn-Al-Mg-based alloy coated layer. The average of the three samples is then used as the coating weight per surface. [0063] In this embodiment, as a lower or upper layer of the Zn-Al-Mg-based alloy coated layer, an additional layer may be provided according to the purpose without deteriorating the actions and effects of the present disclosure. Examples of the lower layer include a nickel pre-coated layer. Examples of the upper layer include a chemical conversion treatment layer containing, for example, a zirconium oxide or a zirconium-titanium oxide.

**EXAMPLES** 

**[0064]** The base steel sheets used were cold-rolled steel sheets ( $Ac_3 = 814 \,^{\circ}\text{C}$ ) of 1.4 mm thick, each having a chemical composition containing, in mass%, C: 0.23 %, Si: 0.25 %, Mn: 1.2 %, P: 0.005 %, S: 0.001 %, Al: 0.03 %, N: 0.004 %, Nb: 0.02 %, Ti: 0.02 %, B: 0.002 %, Cr: 0.2 %, and Sb: 0.008 %, with the balance being Fe and inevitable impurities. **[0065]** The cold-rolled steel sheets were immersed in a hot-dip Zn-Al-Mg-based coating bath with a predetermined chemical composition at a predetermined bath temperature in a galvanizing line, and then subjected to N<sub>2</sub> gas wiping, to produce coated steel sheets for hot press forming, which are labeled No. 1 to No. 14 in Table 1. Table 1 lists the Al

content, the Mg content, and the content of other elements, as well as the liquidus temperature in an air atmosphere for each Zn-Al-Mg-based alloy coated layer. The content of each element and the liquidus temperature were controlled by adjusting the chemical composition of the coating bath. The content of each element in the coated layer was determined by quantitative analysis of each component of the coated layer contained in the hydrochloric acid exfoliation solution using ICP-AES. The liquidus temperature of the coated layer was determined by the above-mentioned method. Table 1 also lists the coating weight per surface of the Zn-Al-Mg-based alloy coated layer as determined by the above-described method. The coating weight was controlled by adjusting the wiping gas flow rate and the line speed.

**[0066]** Then, the steel sheets for hot press forming thus obtained were subjected to hot press forming. Specifically, from each obtained steel sheet for hot press forming, a test specimen of  $150 \text{ mm} \times 300 \text{ mm}$  was taken and subjected to heat treatment in an electric furnace. The heat treatment conditions (heating temperature and holding time) are listed in Table 1. After the heat treatment, each test specimen was removed from the electric furnace and immediately subjected to hot press forming at a forming start temperature of  $700 \,^{\circ}\text{C}$  using a hat-shaped press mold to obtain a hot pressed member. The shape of each obtained hot pressed member was  $100 \,^{\circ}\text{mm}$  in flat length on the top surface,  $50 \,^{\circ}\text{mm}$  in flat length on the side surfaces, and  $50 \,^{\circ}\text{mm}$  in flat length on the bottom surface. The bending radius (or bending R) of the press mold was 7R for each shoulder on both the top and bottom surfaces.

(Evaluation of Fe-Zn-Al-Mg-based Alloy Coated Layer/Oxide layer of Hot Pressed Member)

[0067] From a flat part on the top surface of each obtained hot pressed member, a test specimen was taken for cross-sectional observation, and a cross-section of the Fe-Zn-Al-Mg-based alloy coated layer was observed under SEM. In each sample,  $\alpha$ -Fe and  $\Gamma$  phases could be distinguished from each other by their distinctly different contrasts in the cross-sectional SEM image. FIG. 1 illustrates a cross-sectional SEM image of the Fe-Zn-Al-Mg-based alloy coated layer of the hot pressed member indicated by No. 2, which represents one of our examples, and FIG. 2 illustrates a cross-sectional SEM image of the Fe-Zn-Al-Mg-based alloy coated layer of the hot pressed member indicated by No. 8, which represents one of comparative examples. In FIG. 1, precipitation of the  $\Gamma$  phase is suppressed, and the  $\Gamma$  phase is scattered discontinuously in the  $\alpha$ -Fe phase. In contrast, in FIG. 2, precipitation of the  $\Gamma$  phase is more significant, and the  $\Gamma$  phase is present in the form of continuous planes. In addition, I $_{\Gamma}$  and I $_{\alpha}$  were measured by X-ray diffraction using a Co-K $\alpha$  (wavelength: 1.79021 Å) radiation source at an incident angle of 25°, where Ir is an intensity of a diffraction peak of (411) plane of the  $\Gamma$  phase present in an angular range of 41.5°  $\leq$  20  $\leq$  43.0° and I $_{\alpha}$  is an intensity of a diffraction peak of (110) plane of the  $\alpha$ -Fe phase present in an angular range of 51.0°  $\leq$  20  $\leq$  52.0°. Table 1 lists the ratio of I $_{\Gamma}$ /I $_{\alpha}$ . X-ray diffraction measurements were performed using a curved IP X-ray diffractometer (RINT-RAPID II-R available from Rigaku Corporation), under a set of conditions including tube voltage of 45 kV, tube current of 160 mA, integration time of 600 sec, and collimator diameter of 3 mm.

**[0068]** For each sample, the Al and Mg concentrations in the oxide layer were measured by the above-mentioned method, and the results are listed in Table 1. In addition, for each sample, the coating weight per surface of the Fe-Zn-Al-Mg-based alloy coated layer was measured by the above-mentioned method, and the results are listed in Table 1.

(Evaluation 1: Painting Layer Adhesion)

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40 [0069] A test specimen of 70 mm × 150 mm was cut from a flat part on the top surface of each obtained hot pressed member, and subjected to zirconium-based chemical conversion treatment. Specifically, the chemical conversion treatment was performed using commercially available chemical conversion treatment liquid (zirconium-based chemical conversion treatment: Palmina 2100, available from Nihon Parkerizing Co. Ltd.) under a set of conditions including bath temperature of 35°C and treatment time of 120 seconds. Then, each test specimen was energized under the voltage condition that the voltage was raised in 30 seconds and held at a constant voltage for 150 seconds such that a painting layer having a thickness of 1.5 μm would be formed after baking with commercially available cationic electrodeposition paint, and then baked in an electric furnace at an ambient temperature of 170 °C for 20 minutes. The cationic electrodeposition paint used was Electron GT-100 V-1 Gray, available from Kansai Paint Co. Ltd.

**[0070]** Eleven cuts reaching the base steel sheet were made on each test specimen after electrodeposition painting with a cutter knife at intervals of 1 mm in each of the longitudinal and transverse directions to make one hundred grid squares on a surface of the test specimen. The cellophane tape<sup>®</sup> ("cellophane tape" is a registered trademark in Japan, other countries, or both) was strongly pressed onto the grid, and the edge of the tape was pulled off at once at a 45° angle. The number of grid squares of the painting layer that were peeled off from the surface of each test specimen was counted and judged according to the criteria shown below, with Excellent or Good being accepted. The evaluation results are presented in Table 1.

Excellent: the number of grid squares peeled off = 0

## (continued)

Good: the number of grid squares peeled off = 1
Fair: the number of grid squares peeled off = 2 to 5
Poor: the number of grid squares peeled off = more than 5

(Evaluation 2: Post-painting Corrosion Resistance)

**[0071]** Test specimens were prepared in the same way as in Evaluation 1 until the step of electrodeposition painting, and the 7.5 mm edge of the evaluation surface and the non-evaluation surface (rear side) of each test specimen were sealed with tape. Then, a cross-cut scratch of 60 mm in length and 60° center angle was made in the center of the evaluation surface with a cutter knife to a depth that reached the base steel sheet. Each obtained test specimen was subjected to a corrosion test (VDA 233-102) and evaluated according to the corrosion condition after 4 weeks.

**[0072]** The maximum swelling width on one side from the crosscut was measured and judged according to the criteria shown below, with Excellent or Good being accepted. The evaluation results are presented in Table 1.

Excellent:	maximum swelling width on one side = less than 1.5 mm
Good:	maximum swelling width on one side = 1.5 mm or more and less than 3.0 mm
Fair:	maximum swelling width on one side = 3.0 mm or more and less than 4.0 mm

Poor: maximum swelling width on one side = 4.0 mm or more

5		Classification			Comparative Example	Example	Example	Comparative Example	Example	Example	Example	Comparative Example	Comparative Example	Example	Example	Example	Example	Example			
10		Evaluation results	on results	on results	on results	Post-paint-	ing corro- sion resist- ance	Fair	Excellent	Excellent	Poor	Excellent	Excellent	Good	Poor	Fair	Excellent	Excellent	Excellent	Excellent	Excellent
		Evaluati	Daipting	layer ad- hesion	Excellent	Excellent	Good	Poor	Excellent	poog	Excellent	Poor	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent			
15		Hot pressed member	Oxide layer	AI + Mg (atomic%)	30	37	30	15	37	30	42	10	35	31	35	40	35	40			
20			t pressed r	t pressed r	t pressed r	Coated layer	Coating weight (g/m²)	06	180	240	009	270	360	20	150	180	180	180	180	180	180
		Н	Coat	$I_{\Gamma}/I_{\alpha}$	8.0	0.3	1.0	0.1	9.0	0.2	1.0	09	9.0	0.3	0.3	6.0	6.0	0.3			
25		efore hot orming	PaiploH	time (min)	1	1	2	2	1	9	l	1	1	1	1	1	1	1			
30	Table 1	Heating before hot press forming	Heating b press f	Heating b	Heating	temp. (°C)	800	950	950	1050	950	026	026	950	950	950	950	950	950	950	
35			r hot press forming	Steel sheet	$Ac_3$ Transformation point (°C)	814	814	814	814	814	814	814	814	814	814	814	814	814	814		
40		Steel sheet for hot press forming			Coating weight (g/m²)	09	60	60	60	90	06	35	60	60	60	60	60	60	60		
				r hot press		Liquidus temp. (°C)	383	383	383	383	383	383	383	417	405	385	385	385	385	385	
45				Coated layer	Optional element (mass%)	-	-	-	-	-	-	-	1	-	-	Cr, 0.05 %	Cr, 0.5 %	Ni, 0.05 %	Ni, 0.5 %		
50				St	O	Mg con- tent (mass%)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.0	0.3	0.7	0.7	2.0	0.7	0.7	
55				Al content (mass%)	4	4	4	4	4	4	4	0.2	7.5	9	9	9	9	9			
		o Z			-	2	3	4	2	9	7	8	6	10	11	12	13	14			

**[0073]** It can be seen from the results in Table 1 that each of the hot pressed members in our examples has excellent painting layer adhesion and post-painting corrosion resistance when subjected to electrodeposition painting after zirconium-based chemical conversion treatment.

#### 5 INDUSTRIAL APPLICABILITY

**[0074]** The hot pressed member according to the present disclosure is suitable for automotive undercarriage parts and automotive body structural parts.

Claims

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1. A hot pressed member comprising:

a base steel sheet:

a Fe-Zn-Al-Mg-based alloy coated layer containing an  $\alpha$ -Fe phase and a  $\Gamma$  phase and formed on at least one surface of the base steel sheet at a coating weight per surface of 40 g/m² to 400 g/m²; and an oxide layer containing Zn, Al, and Mg and formed on the Fe-Zn-Al-Mg-based alloy coated layer, wherein a ratio of I $_{\Gamma}$ /I $_{\alpha}$  is 0.5 or less when measured by X-ray diffraction using a Co-K $\alpha$  (wavelength: 1.79021 Å) radiation source at an incident angle of 25°, where Ir is an intensity of a diffraction peak of (411) plane of the  $\Gamma$  phase present in an angular range of 41.5°  $\leq$  20  $\leq$  43.0° and I $_{\alpha}$  is an intensity of a diffraction peak of (110) plane of the  $\alpha$ -Fe phase present in an angular range of 51.0°  $\leq$  20  $\leq$  52.0°, and a sum of Al and Mg concentrations in the oxide layer is 28 atomic% or more.

2. A method of producing a hot pressed member, the method comprising:

heating a coated steel sheet for hot press forming to a temperature range of Ac<sub>3</sub> transformation point to 1000 °C, the coated steel sheet for hot press forming comprising:

a base steel sheet; and

a Zn-Al-Mg-based alloy coated layer formed on at least one surface of the base steel sheet at a coating weight per surface of  $30 \text{ g/m}^2$  to  $180 \text{ g/m}^2$ , having a chemical composition containing, in mass%, Al: 3% to 10% and Mg: 0.2% to 0.8%, with the balance being Zn and inevitable impurities, and having a liquidus temperature in an air atmosphere of 400% C or lower, and

then subjecting the coated steel sheet to hot press forming.

- 3. The method of producing a hot pressed member according to claim 2, wherein the chemical composition of the Zn-Al-Mg-based alloy coated layer further contains at least one selected from the group consisting of Ca, Sr, Mn, V, Cr, Mo, Ti, Ni, Co, Sb, Zr, and B in a total amount of 1 mass% or less.
- **4.** A coated steel sheet for hot press forming comprising:

a base steel sheet; and

a Zn-Al-Mg-based alloy coated layer formed on at least one surface of the base steel sheet at a coating weight per surface of 30 g/m² to 180 g/m², having a chemical composition containing, in mass%, Al: 3 % to 10 % and Mg: 0.2 % to 0.8 %, with the balance being Zn and inevitable impurities, and having a liquidus temperature in an air atmosphere of 400 °C or lower.

5. The coated steel sheet for hot press forming according to claim 4, wherein the chemical composition of the Zn-Al-Mg-based alloy coated layer further contains at least one selected from the group consisting of Ca, Sr, Mn, V, Cr, Mo, Ti, Ni, Co, Sb, Zr, and B in a total amount of 1 mass% or less.

FIG. 1

 $\Gamma - Fe_3Zn_{10}$  phase Solute ( $\alpha - Fe$ ) phase

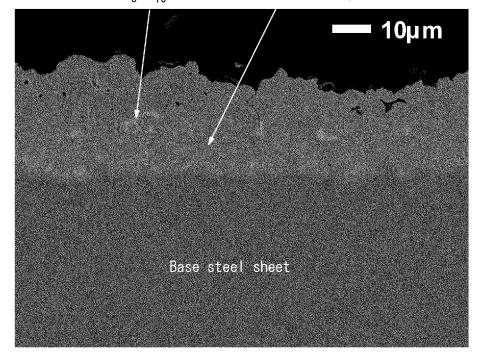
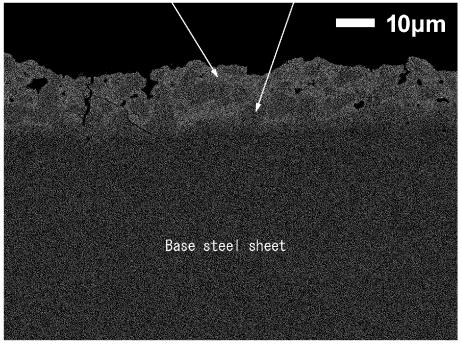


FIG. 2

 $\Gamma$ -Fe<sub>3</sub>Zn<sub>10</sub>phase Solute ( $\alpha$ -Fe) phase



International application No.

INTERNATIONAL SEARCH REPORT

5 PCT/JP2020/040696 A. CLASSIFICATION OF SUBJECT MATTER C23C 2/06(2006.01)i; B21D 22/20(2006.01)i; C21D 1/18(2006.01)i; C21D 9/00(2006.01)i; C22C 18/04(2006.01)i; C23C 2/28(2006.01)i; C22C 38/00(2006.01)n; C22C 38/60(2006.01)n C23C2/06; B21D22/20 H; C21D1/18 C; C21D9/00 A; C22C18/04; 10 C23C2/28; C22C38/00 301Z; C22C38/60 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) C23C2/06; B21D22/20; C21D1/18; C21D9/00; C22C18/04; C23C2/28; C22C38/00; C22C38/60 15 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Published examined utility model applications of Japan 1922-1996 Published unexamined utility model applications of Japan 1971-2020 Registered utility model specifications of Japan 1996-2020 Published registered utility model applications of Japan 1994-2020 20 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) DOCUMENTS CONSIDERED TO BE RELEVANT Category\* Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. JP 2013-241671 A (NISSHIN STEEL CO., LTD.) 05 4-5 Χ Υ December 2013 (2013-12-05) claims, paragraphs 1 - 525 [0001]-[0123] WO 2014/122900 A1 (JFE STEEL CORPORATION) 14 Χ August 2014 (2014-08-14) paragraphs [0001]-[0004], 1-5 [0069]-[0070] 30 JP 2001-348678 A (NISSHIN STEEL CO., LTD.) 18 Χ 4 December 2001 (2001-12-18) paragraphs [0021], [0027], [0029], [0033] JP 2005-113233 A (NIPPON STEEL CORP.) 28 April 1 - 5Υ 2005 (2005-04-28) paragraphs [0001]-[0016] 35 JP 2012-112010 A (JFE STEEL CORPORATION) 14 June 1 - 5Υ 2012 (2012-06-14) paragraphs [0001]-[0016]  $\bowtie$ Further documents are listed in the continuation of Box C. See patent family annex. 40 Special categories of cited documents later document published after the international filing date or priority "A" document defining the general state of the art which is not considered to be of particular relevance date and not in conflict with the application but cited to understand the principle or theory underlying the invention "E" earlier application or patent but published on or after the international document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document of particular relevance; the claimed invention cannot be 45 considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "O" document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than document member of the same patent family the priority date claimed Date of mailing of the international search report Date of the actual completion of the international search 15 December 2020 (15.12.2020) 22 December 2020 (22.12.2020) 50 Name and mailing address of the ISA/ Authorized officer Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan Telephone No. Form PCT/ISA/210 (second sheet) (January 2015)

5	INTERNATIONAL SEARCH REPORT	International application No.
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## REFERENCES CITED IN THE DESCRIPTION

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