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(54) METHOD OF MELTING ALLOY CONTAINING HIGH-VAPOR-PRESSURE METAL

VERFAHREN ZUM SCHMELZEN VON LEGIERUNGEN MIT METALL MIT HOHEM DAMPFDRUCK
PROCÉDÉ DE FUSION D'UN ALLIAGE CONTENANT UN MÉTAL HAUTE PRESSION DE VAPEUR

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Description

Indication of the related application:

5 **[0001]** The present application is an application claiming priority of JP 2005-56985 filed on March 2, 2005.

TECHNICAL FIELD

10 **[0002]** This invention relates to a melting method wherein an alloy containing a metal of a low melting point, a low boiling point and a high vapor pressure such as Mg, Ca, Li, Zn, Mn, Sr or the like is produced by melting.

RELATED ART

15 **[0003]** The metal such as Mg, Ca, Zn, Li or the like or an alloy including such a metal is widely expected for applications as a structural material or a functional material because the weight is light and the specific strength is high as compared with a transition metal such as iron or the like or an alloy thereof. Among them, Mg and Ca are richly existent in earth crust and sea water and low in the cost and have no harmful influence upon human body, so that they are expected to be expanding applications.

20 **[0004]** However, the metals such as Mg, Ca, Zn, Li and the like and alloys thereof are low in the melting point or boiling point and high in the vapor pressure, so that if it is intended to produce the alloys containing these metals by a melting method, there is a problem that the inside of the melting furnace is contaminated with metal fine powder generated by vaporization. Particularly, since Mg is very active, if it adheres to an inner wall or the like of the melting furnace and is exposed to an atmosphere, there is a high risk of causing fire, explosion or the like.

25 **[0005]** Also, there is a problem that the fume of the vaporized metal fine powder contaminates a window for visual observation of the melting furnace or shields a visual range and hence whether or not the alloy is completely melted and whether or not the stirring is sufficient cannot be visually confirmed or judged. Furthermore, the estimation of exact vaporization amount becomes difficult, so that there is a problem that the alloy having a targeted chemical composition cannot be produced.

30 **[0006]** Moreover, the alloy containing Mg, Ca, Zn, Li or the like can be produced by a mechanical alloying method such as ball milling or the like in addition to the melting method. Since such a method is a production method without melting the starting metals, the above problem will not be caused by the generation of the metal fine powder, but there is still a problem that the contamination due to the incorporation of iron and the like from the mill pot and the deterioration of the alloy homogeneity occur. Also, the long time is taken in the production, causing a problem that the production cost is high. Therefore, this method is not suitable in the mass production.

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DISCLOSURE OF THE INVENTION

40 **[0007]** As mentioned above, the conventional methods for the production of the alloys containing Mg, Ca, Zn, Li and the like have various problems, so that a new production method without such problems is strongly required. Therefore, it is an object of the invention to propose a useful melting method for the production of an alloy containing a metal of a low melting point, a low boiling point and a high vapor pressure.

[0008] It is another object of the invention to propose a method of safely producing a greater amount of an alloy having a targeted chemical composition in a higher precision while reducing the risk of firing, contamination or the like by active metal fine powder being vaporized.

45 **[0009]** The inventors have made various studies in order to achieve the above objects. As a result, it has been found out that it is effective to rationalize a gas component constituting the melting atmosphere, and particularly use helium gas, and the invention has been accomplished.

50 **[0010]** That is, the invention lies in a method of producing an alloy containing a high vapor pressure metal by melting an alloy containing one or more of Mg, Ca, Li, Zn, Mn and Sr, characterized in that a helium containing gas is used as an atmosphere gas for the melting.

[0011] In the invention, a helium concentration in the atmosphere gas is not less than 10 vol%, and it is preferable that the atmosphere gas is a mixed gas of helium and a gas not reacting with the starting metal such as nitrogen, argon or the like. The pressure of the atmosphere gas is 0.01 MPa -1 MPa.

55 **[0012]** According to the method of the invention having the above construction, an alloy containing a low melting point, a boiling point and a high vapor pressure metal such as Mg, Ca, Li, Zn or the like, for example, an alloy of the above metal and Al, Ni or the like can be precisely and safely produced as an alloy having a targeted chemical composition in a greater amount at a low cost without causing the risk of firing, contamination or the like by active metal fine powder being vaporized.

[0013] Furthermore, the melting method of the invention using the helium containing gas as an atmosphere gas can solve the problems due to the above active metal fine powder but also has a feature that the solidification rate of the molten metal is enhanced by a high thermal conductivity inherent to the helium gas or the effect of quench-solidification is obtained. Therefore, according to the method of the invention, a special alloy conventionally produced by using a melting apparatus for an exclusive use of quench-solidification can be produced even by using the usual melting apparatus.

[0014] As seen from the above, the development and practical application of structural materials or functional materials made from light weight metal or alloy thereof, which will be used in the new generation, can be expected to be largely advanced by using the melting method according to the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015]

FIG. 1 is a graph showing an influence of a helium gas concentration in an atmosphere gas upon a melting yield of Mg in the melting of CaMg_2 alloy.

FIG. 2 is a view comparing X-ray diffraction curves of alloys obtained when helium gas and argon gas are used as an atmosphere gas in the melting of CaMg_2 alloy.

FIG. 3 is a view comparing pressure-composition isothermal curves of La-Ni based hydrogen storage alloy melted in a helium gas atmosphere and La-Ni based hydrogen storage alloy melted in an argon gas atmosphere.

BEST MODE FOR CARRYING OUT THE INVENTION

[0016] The melting method according to the invention will be described in detail below.

[0017] The melting method according to the invention lies in a point that a helium containing gas is used as an atmosphere gas for the melting of an alloy containing at least one metal of a low melting point, a low boiling point and a high vapor pressure such as Mg, Ca, Li, Zn and the like. When the helium containing gas is used as the melting atmosphere, it is possible to prevent metal fine powder generated by vaporization in the melting from segregation and the risk of firing or the like due to the segregate of the metal fine powder or the contamination can be largely reduced but also the alloy having the target chemical composition can be safely produced at a greater amount in a high precision.

[0018] It is considered that the above effect of the helium containing gas can be obtained due to the fact that helium is high in the thermal conductivity (about 3 times of argon), low in the density (0.1 times of argon) and long in the average free stroke (about 3 times of argon) as compared with the other inert gas. Moreover, hydrogen has the features similar to those of helium, but hydrogen is not suitable as the melting atmosphere gas because it may react with the starting metal to form a metal hydride. However, if it is intended to melt a metal not reacting with hydrogen and having a low melting point, a low boiling point and a high vapor pressure, when a hydrogen containing gas is used as an atmosphere gas, the effect similar to that in the use of helium can be expected.

[0019] Helium gas is very expensive. Therefore, the helium gas is preferably replaced partially with a cheap gas not reacting with the starting metal from a viewpoint of the cost reduction. The inventors have made experiments of replacing helium with various other gases and found out that when a part of helium gas is replaced with a gas not reacting with the starting metal such as nitrogen, argon or the like, the risk of firing or the like due to the segregation of the metal fine powder generated by vaporization and the contamination thereof can be fairly reduced.

[0020] Moreover, as a gas replacing helium gas, an argon gas is most preferable. Because, the argon gas is cheap and does not react with Mg, Ca, Li, Zn and the like even at a higher temperature.

[0021] However, it has been confirmed that there is a limit in replacing helium with the other inert gas. According to the inventors' knowledge, the helium content in such a mixed gas is required to be at least 10 vol%, and is preferably not less than 25 vol% and more preferably not less than 50 vol%. It is further preferably not less than 95 vol%, and may be naturally 90-100 vol%. Thus, the reason why the lower limit of the ratio of helium occupied as the atmosphere gas is 10 vol% is due to the fact that when it is less than 10 vol%, the aforementioned action and effect of helium are not obtained.

[0022] In the melting method according to the invention, a pressure of the melting atmosphere comprising the helium containing gas is 0.01 MPa - 1 MPa. When the pressure is less than 0.01 MPa, the vaporization temperature is considerably decreased, the vaporization is promoted, and the amount of the metal fine powder generation cannot be decreased. While, when it exceeds 1 MPa, the vaporization amount decreases, but the melting point rises and the melting becomes difficult.

[0023] Moreover, the pressure range of the helium containing gas means a pressure at room temperature before the melting and there may be a case exceeding the above range when the temperature inside the furnace becomes higher in the melting procedure.

[0024] Also, the optimum ranges of the concentration and pressure of helium used as the atmosphere gas are mainly obtained as a result of consideration and development from a viewpoint of the cost.

[0025] In the melting method of the invention, impurity gases such as oxygen, carbon dioxide, steam and the like may be included in the helium containing gas supplied as an atmosphere gas within a scope not damaging the action of the invention. In this case, the content is preferably not more than 1 mass%. When it exceeds 1 mass%, these gases react with Mg, Ca, Li, Zn and the like to produce an oxide, a hydroxide, a carbide and the like and hence there cannot be produced an alloy having a targeted chemical composition and a compound.

EXAMPLES

[0026] The invention will be described in detail with reference to the following examples, but the invention is not naturally limited to these examples.

(Invention Example 1)

[0027] As a starting material for hydrogen storage alloy CaMg_2 , 1 kg in total of Mg and Ca metals are provided so as to have a molar ratio of 2:1, and these metals are charged into an induction melting type melting furnace, and thereafter the interior of the furnace is evacuated to 8×10^{-3} Torr and then helium gas (concentration: 100 vol%) is introduced thereinto up to 600 Torr as an atmosphere gas. Next, the melting furnace is heated up to a temperature of 1100°C while filling the inside of the furnace with the atmosphere gas to melt the starting materials, and further kept for 30 minutes while maintaining a melting temperature of the resulting alloy at 1050°C . Thereafter, the molten alloy is poured onto a water-cooled mold platen and solidified by cooling at a cooling rate of $1000^\circ\text{C}/\text{sec}$ to prepare CaMg_2 alloy. With respect to thus obtained CaMg_2 alloy, the melting yield and chemical composition are measured by the following methods (1) and (2).

(1) Measurement of melting yield

[0028] The mass of the starting material before melting and the mass of alloy after melting to mold are measured to determine the decreased mass by vaporization and calculate the melting yield.

(2) Measurement of chemical composition

[0029] The chemical composition of the alloy after melting to mold is quantitatively analyzed by ICP emission spectroscopy.

[0030] The measured results are shown in Table 1. As seen from these results, in Invention Example 1 using helium gas as a melting atmosphere gas, the melting yield is as high as not less than 98.2%, and further the alloy can be produced in a high precision within $\pm 1\%$ with respect to the targeted alloy composition.

Table 1

	He concentration in atmosphere gas (vol%)	Targeted chemical composition	Analytical result of chemical composition	Melting yield (%)
Invention Example 1	100	CaMg_2	$\text{CaMg}_{1.98}$	98.25
Invention Example 2	75	CaMg_2	$\text{CaMg}_{1.96}$	97.84
Invention Example 3	50	CaMg_2	$\text{CaMg}_{1.93}$	97.54
Invention Example 4	25	CaMg_2	$\text{CaMg}_{1.91}$	97.27
Invention Example 5	100	CaAl_2	$\text{CaAl}_{2.02}$	98.14
Invention Example 6	100	MgNi_2	$\text{MgNi}_{1.96}$	97.87

(continued)

	He concentration in atmosphere gas (vol%)	Targeted chemical composition	Analytical result of chemical composition	Melting yield (%)
Invention Example 7	100	CaNi ₂	CaNi _{2.04}	97.81
Comparative Example 1	0	CaMg ₂	CaMg _{1.77}	96.40

(Comparative Example 1)

[0031] CaMg₂ alloy is prepared in the same manner as in Invention Example 1 except that argon gas (concentration: 100 vol%) is used as an atmosphere gas. With respect to this alloy, the melting yield and chemical composition are measured by the above methods (1) and (2) to obtain the results shown in Table 1.

(Invention Examples 2-4)

[0032] CaMg₂ alloys are prepared in the same manner as in Invention Example 1 except that the concentration of helium gas introduced as an atmosphere is changed to 75, 50 and 25 vol% (remainder is argon gas), respectively. With respect to these CaMg₂ alloys, the melting yield and chemical composition are measured by the above methods (1) and (2) to obtain the results shown in Table 1. As seen from these results, when the helium gas concentration exceeds 50 vol% (Invention Examples 2 and 3), the melting yield is as high as about 98% and the targeted alloy composition can be obtained in a high precision. On the other hand, when the helium gas concentration is 25 vol% (Invention Example 4), the melting yield and the alloy composition are inferior to those of Invention Examples 1-3, but the melting yield and the precision of the alloy composition are improved as compared with the case of using no helium gas (Comparative Example 1), from which the effect by the introduction of helium gas can be confirmed.

[0033] A relationship between the helium gas concentration and the melting yield obtained from the results of Invention Examples 1-4 and Comparative Example 1 is shown in FIG. 1. As seen from FIG. 1, the melting yield is improved as the helium gas concentration becomes higher.

[0034] Further, the measurement of X-ray diffraction intensity is carried out with respect to CaMg₂ alloys obtained in Invention Example 1 and Comparative Example 1 to confirm whether or not the alloy and compound have a targeted single-phase structure. The results are shown in FIG. 2. As seen from FIG. 2, the CaMg₂ alloy of Invention Example 1 is an alloy of single CaMg₂ phase structure, while the alloy of Comparative Example 1 is an alloy of two mixed phase structure consisting of CaMg₂ phase and Ca phase.

[0035] As seen from Table 1 and FIGS. 1 and 2, according to the method of the invention, it is possible to produce a single-phase alloy having a targeted composition without variations. On the contrary, according to the method of the comparative example, the evaporation loss of the starting materials cannot be controlled and the composition is largely shifted from the targeted composition. Furthermore, the variations of the alloy composition are caused.

(Invention Example 5)

[0036] CaAl₂ alloy is prepared in the same manner as in Invention Example 1 except that Ca and Al are used as a starting material, and the melting yield and chemical composition of the resulting CaAl₂ alloy are measured by the above methods (1) and (2) to obtain results shown in Table 1. As seen from these results, in Invention Example 5, the melting yield is as high as about 98% and the target alloy is obtained in a high precision within $\pm 1\%$ with respect to the targeted Al composition.

(Invention Example 6)

[0037] MgNi₂ alloy is prepared in the same manner as in Invention Example 1 except that Mg and Ni are used as a starting material, and the melting yield and chemical composition of the resulting MgNi₂ alloy are measured by the above methods (1) and (2) to obtain results shown in Table 1. As seen from these results, in Invention Example 6, the melting yield is as high as about 98% and the target alloy is obtained in a high precision within $\pm 2\%$ with respect to the targeted Ni composition.

(Invention Example 7)

[0038] CaNi₂ alloy is prepared in the same manner as in Invention Example 1 except that Ca and Ni are used as a starting material, and the melting yield and chemical composition of the resulting CaNi₂ alloy are measured by the above methods (1) and (2) to obtain results shown in Table 1. As seen from these results, in Invention Example 7, the melting yield is as high as about 98% and the target alloy is obtained in a high precision within $\pm 2\%$ with respect to the targeted Ni composition.

(Invention Example 8 and Comparative Example 2)

[0039] A pressure-composition isothermal curve is measured with respect to a La-Ni based hydrogen storage alloy produced by melting in an atmosphere of 100 vol% helium gas according to the invention (Invention Example 8) and a La-Ni based hydrogen storage alloy produced by melting in an atmosphere of 100 vol% argon gas (Comparative Example 2) to obtain results shown in FIG. 3. As seen from FIG. 3, the alloy of Invention Example 8 is flat and wide in the plateau region as compared with the alloy of Comparative Example 2, and the alloy of Invention Example 8 quench-solidified with the helium gas is an alloy having an excellent homogeneity.

INDUSTRIAL APPLICABILITY

[0040] The technique of the invention can be utilized as a mass production technique for alloys containing a metal of a low melting point, a low boiling point and a high vapor pressure such as Mg, Ca, Zn, Li or the like but also can be applied to the melting of single body made of each of these metals, the melting of a compound used in semiconductors or the like such as gallium-arsenic or other compounds. Furthermore, the invention is applicable to a melting technique of structural materials, functional materials, semiconductor compounds, and other compounds made from a light metal or alloy used in the new generation.

Claims

1. A method of melting an alloy containing a metal of a high vapor pressure **characterized in that** as the method for melting to produce an alloy containing one or more of Mg, Ca, Li, Zn, Mn and Sr, a gas containing helium of not less than 10 vol% is used as an atmosphere gas under an atmosphere gas pressure of 0.01 - 1 MPa for the melting.
2. A method for melting an alloy containing a metal of a high vapor pressure according to claim 1, wherein the atmosphere gas is a mixed gas of helium and a gas not reacting with the starting metal such as nitrogen or argon.

Patentansprüche

1. Verfahren zum Schmelzen einer Legierung, die ein Metall mit hohem Dampfdruck enthält, **dadurch gekennzeichnet, dass** als das Schmelzverfahren zur Herstellung einer Legierung, die ein oder mehrere von Mg, Ca, Li, Zn, Mn und Sr enthält, ein Gas, das nicht weniger als 10 Vol.-% Helium enthält, als Atmosphärendruckgas unter einem Atmosphärendruck von 0,01 - 1 MPa zum Schmelzen verwendet wird.
2. Verfahren zum Schmelzen einer Legierung, die ein Metall mit hohem Dampfdruck enthält, nach Anspruch 1, worin das Atmosphärendruckgas ein gemischtes Gas aus Helium und einem nicht mit dem Ausgangsmetall reagierendes Gas, wie Stickstoff oder Argon, ist.

Revendications

1. Procédé de fusion d'un alliage contenant un métal à pression de vapeur élevée **caractérisé en ce que** dans le procédé de fusion pour produire un alliage contenant un ou plusieurs éléments parmi Mg, Ca, Li, Zn, Mn et Sr, un gaz contenant de l'hélium à pas moins de 10 % en volume est utilisé comme gaz d'atmosphère sous une pression de gaz d'atmosphère comprise entre 0,01 et 1 MPa pour la fusion.
2. Procédé de fusion d'un alliage contenant un métal à pression de vapeur élevée selon la revendication 1, dans lequel le gaz d'atmosphère est un gaz mélangé constitué d'hélium et d'un gaz qui ne réagit pas avec le métal de départ,

tel que l'azote ou l'argon.

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Fig.1

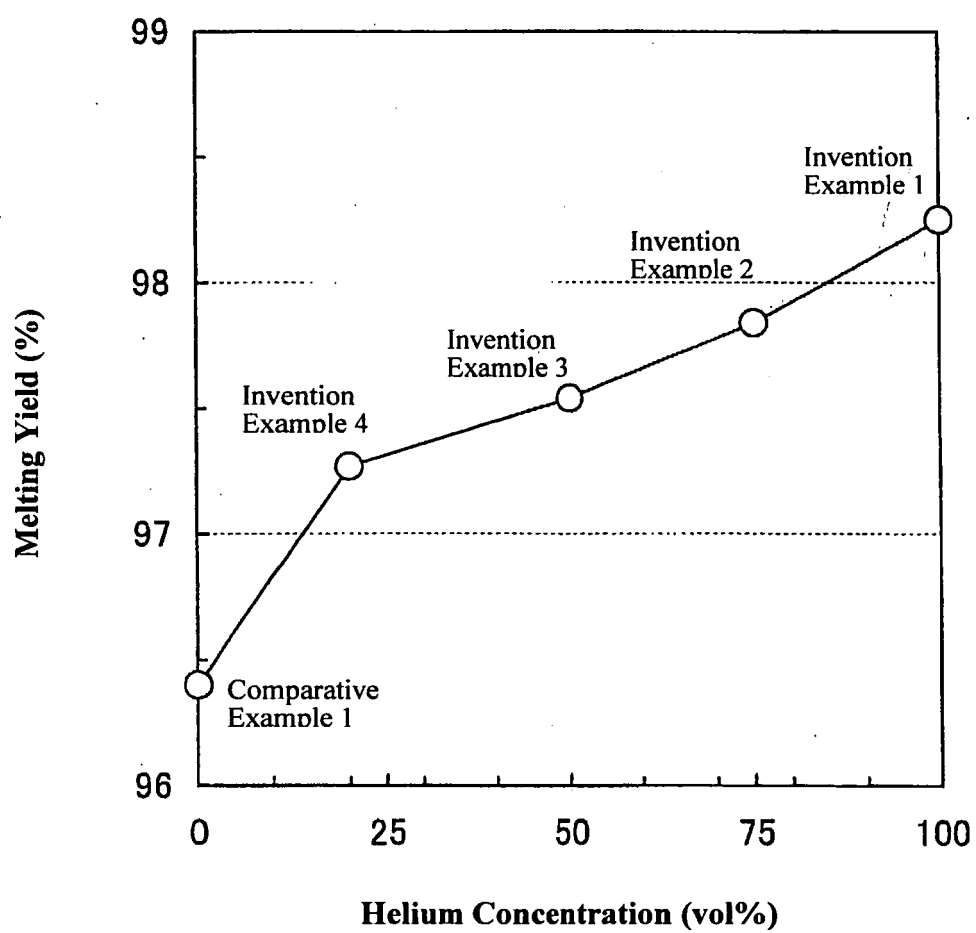


Fig.2

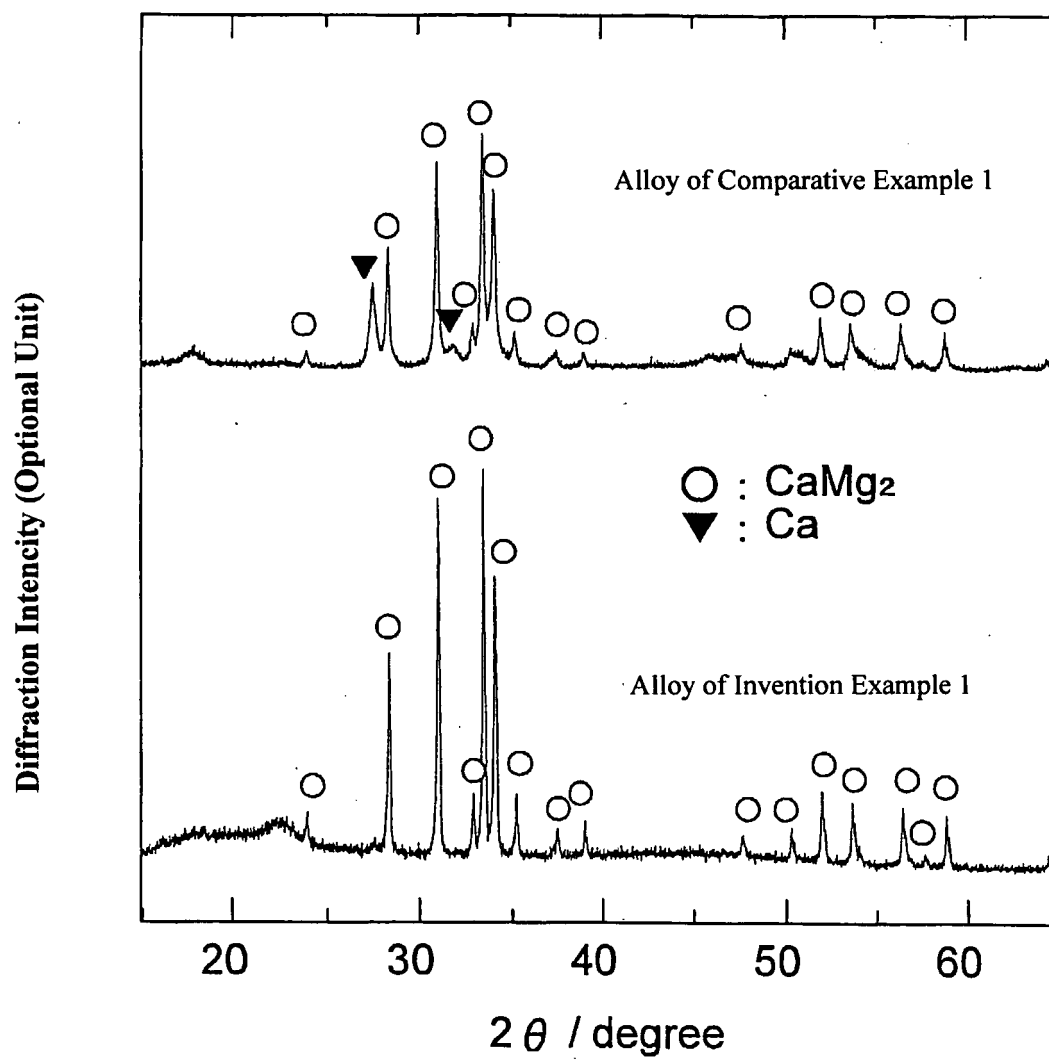
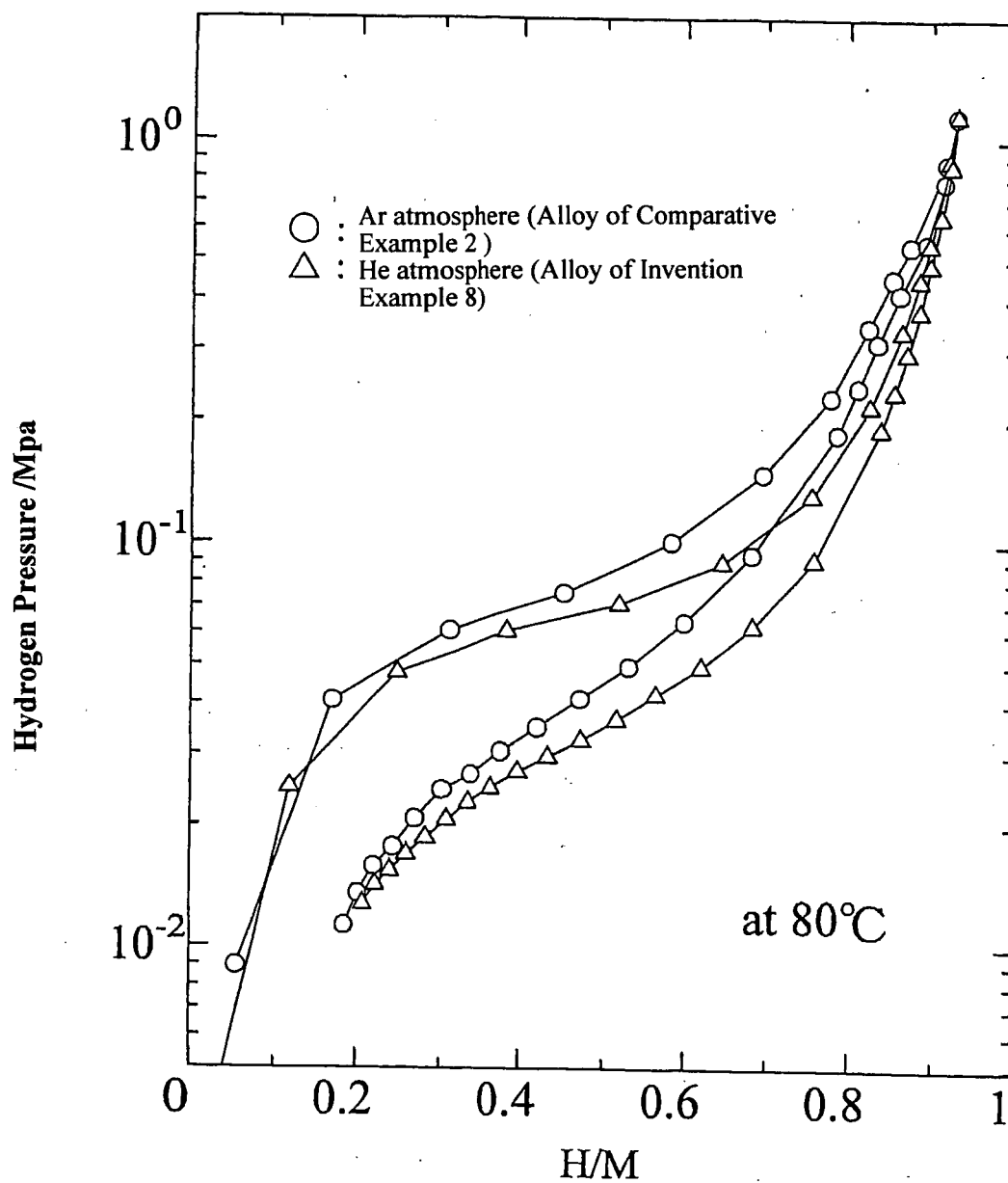


Fig.3



REFERENCES CITED IN THE DESCRIPTION

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