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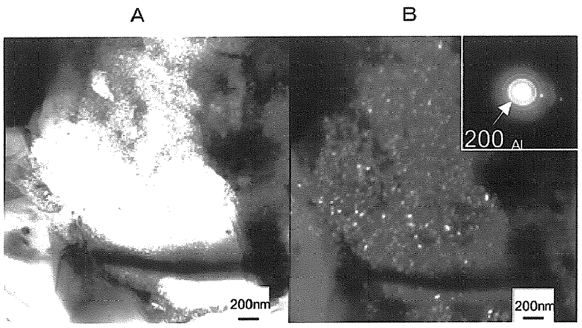
(54) METHOD OF ATOMIZING ALLOY CRYSTAL GRAIN BY HYDROGEN TREATMENT

(57) A technology for atomizing the crystal grains of alloy whose main constituents are elements exhibiting weak affinity with hydrogen. With respect to the alloy whose main constituents are elements exhibiting weak affinity with hydrogen in which an element exhibiting strong affinity with hydrogen is contained, resulting from attaining of presence of an element exhibiting strong affinity with hydrogen in an alloy whose main constituents are elements exhibiting weak affinity with hydrogen, any crystal grains of the alloy can be super-atomized by subjecting the alloy to heat treatment involving hydrogen absorption and release, thereby realizing super-high strength thereof. Thus, the properties of the alloy can be improved and enhanced.

Fig.06



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Description

FIELD OF THE INVENTION

[0001] This invention relates to an alloy whose main constituent(s) is(are) an element(s) weak in affinity for hydrogen and provides a method of refining crystal grains by hydrogen treatment and an alloy effective therefore.

BACKGROUND ART

[0002] Available as a method of improving the mechanical properties and workability of an alloy is refinement of crystal grains of the alloy. Known as techniques for refining crystal grains of an alloy are the combination of cold rolling and recrystallization, the ECAP (Equal Channel Angular Pressing) technique, the technique involving intense strain working such as repeated stack or doubling rolling, the rapid liquid cooling technique or the like, the heat treatment technique involving rapid cooling from an elevated temperature, and the technique comprising heat treatment following mechanical working.

[0003] However, the crystal grain diameter attainable by refining crystal grains using these techniques is about 1 μm, and there is a limit to further improvement in crystal grain refining effect. On the other hand, it is expected that an alloy based on an element(s) weak in affinity for hydrogen, when subjected to crystal grain refinement, will be further strengthened (Fig. 1).

[0004] A method so far reported for crystal grain refinement comprises subjecting a Nd-Fe-B type compound magnet, a Ti-Al-V type alloy, a Mg-Al type alloy or the like based on an element(s) strong in affinity for hydrogen to heat treatment involving absorption and desorption of hydrogen (hydrogen absorption/desorption heat treatment). However, as far as alloys based on an element(s) weak in affinity for hydrogen are concerned, the effectiveness of such method has not been confirmed at all.

DISCLOSURE OF INVENTION

PROBLEMS WHICH THE INVENTION IS TO SOLVE

[0005] It is an object of the present invention to provide a technology of producing an crystal grain refining effect by causing an element strong in affinity for hydrogen to be contained in an alloy based on an element(s) weak in affinity for hydrogen.

[0006] The present inventors made various investigations in an attempt to accomplish the above object and, as a result, found that when an alloy whose main constituent(s) is(are) an element(s) weak in affinity for hydrogen and which contains an element strong in affinity for hydrogen is placed in a hydrogen atmosphere within a temperature range of 0°C to $0.8T_M$ (T_M being the melting point of the metal (or alloy) as expressed in terms of absolute temperature), hydrogen is absorbed into the alloy to become contained therein and the element strong in affinity for hydrogen reacts with the hydrogen thus absorbed.

[0007] Further, they came to realize that when the hydrogen absorbed in the alloy whose main constituent(s) is(are) an element(s) weak in affinity for hydrogen, as indicated by the above finding, is desorbed within a temperature range of 0°C to $0.8T_M$, the crystal grain diameter of the alloy can be reduced to 1 μm or smaller.

[0008] Thus, the alloy system to which such hydrogen absorption/desorption heat treatment can be applied is characterized in that at least one metal strong in affinity for hydrogen as selected from the group consisting of alkali metals such as Li and Na, alkaline earth metals such as Mg and Ca, rare earth metals such as La and Ce, transition metals belonging to the groups 3-5 of the periodic table of the elements, typically Ti and V, and Pd is contained in an alloy based on an element(s) weak in affinity for hydrogen.

[0009] According to the present invention, the following modes of embodiment are provided.

[1] A method of refining crystal grains of an alloy whose main constituent(s) is(are) an element(s) weak in affinity for hydrogen and which contains an element strong in affinity for hydrogen which method is characterized in that the alloy is subjected to hydrogen absorption/desorption heat treatment involving causing the alloy to occlude hydrogen within a temperature range of 0°C to $0.8T_M$ (T_M being the melting point of the metal or alloy as expressed in terms of absolute temperature) and then allowing the hydrogen to be released within a temperature range of 0°C to $0.8T_M$.

[2] A method of refining crystal grains of an alloy as set forth above under [1] which is characterized in that the alloy system to which the hydrogen absorption/desorption heat treatment is applicable is mainly an alloy comprising, as an element(s) weak in affinity for hydrogen, an element or a range of elements selected from elements of the groups 6-10 of the periodic table of the elements (except for Pd), typically Cr, Mn, Fe, Co and Ni, and elements of the groups

11-15 of the periodic table of the elements, typically Cu, Ag, Au, Zn and Al.

[3] A method of refining crystal grains of an alloy as set forth above under [1] or [2] which is characterized in that the alloy system to which the hydrogen absorption/desorption heat treatment is applicable contains at least one metal strong in affinity for hydrogen as selected from the group consisting of alkali metals such as Li and Na, alkaline earth metals such as Mg and Ca, rare earth metals such as La and Ce, transition metals of the groups 3-5 of the periodic table of the elements, typically Ti and V, and Pd.

[4] An alloy consisting of refined crystal grains which is characterized in that it is a product obtained by carrying out a method of refining crystal grains as set forth above under [1]-[3] and consisting of very fine grains refined by the heat treatment of the alloy according to that method.

EFFECTS OF THE INVENTION

[0010] The present invention provides an epoch-making method by which a crystal grain size as small as scores of nanometers to 1 μm can be attained by causing an alloy whose main constituent(s) is(are) an element(s) weak in affinity for hydrogen to absorb and desorb hydrogen; such a small grain size has been regarded as unrealizable in the prior art. The treatment according to the invention can result in refinement of alloy crystal grains and makes it possible to obtain highly strengthened alloy materials and alloy materials improved in workability.

[0011] Other objects, features, superiority and aspects of the present invention will become apparent to those skilled in the art from the description which follows. It is to be understood, however, that the description given herein, including the following description and specific examples, among others, is given for illustrating preferred embodiments of the invention, namely only for the purpose of illustration. Various changes and/or alterations (modifications) within the purport and scope of the invention disclosed herein will be quite obvious to those skilled in the art based on the knowledge obtained from the following description and other parts of the present specification.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012]

[Fig. 1] This figure is a crystal grain diameter-material strength correlation diagram showing that crystal grain refinement can result in further strengthening.

[Fig. 2] This figure shows powder X ray diffraction patterns of an Al-7.8% (by weight) Mg alloy after hydrogen absorption treatment, showing a phase appearing upon that treatment as the function of the treatment temperature.

[Fig. 3] This figure is a powder X ray diffraction pattern of the same Al-7.8% (by weight) Mg alloy after hydrogen absorption treatment, showing a phase appearing upon that treatment as the function of the treatment time.

[Fig. 4] This figure shows transmission electron-micrographs of the Al-7.8% (by weight) Mg alloy after hydrogen absorption treatment, showing the occurrence of a fine MgH_2 phase.

[Fig. 5] This figure shows powder X ray diffraction patterns of the same Al-7.8% (by weight) Mg alloy after hydrogen absorption/desorption treatment, showing a phase appearing upon that treatment as the function of the desorption treatment time.

[Fig. 6] This figure shows transmission electron-micrographs of the Al-7.8% (by weight) alloy after hydrogen absorption/desorption treatment, showing that the metallographic structure of the alloy is refined to about 10 nm.

[Fig. 7] This figure shows powder X ray diffraction patterns of Al-x% (by weight) Mg alloys (x = 3, 5, 7.8) after hydrogen absorption treatment, showing a phase appearing upon that treatment. For all the compositions, an MgH_2 phase appears, indicating that the treatment method in question is effective.

[Fig. 8] This figure shows the change in V content in the mother phase in a Fe-10% (by weight) V alloy after hydrogen absorption treatment as the function of the treatment temperature.

[Fig. 9] This figure is a transmission electron-micrograph of the Fe-10% (by weight) v alloy after hydrogen absorption treatment at 250˚C, indicating the occurrence of fine V-containing precipitates about 10 nm in size.

[Fig. 10] This figure shows powder X ray diffraction patterns of the Fe-10% (by weight) V alloy before treatment, after hydrogen absorption treatment and after hydrogen desorption treatment, respectively.

[Fig. 11] This figure shows powder X ray diffraction patterns of a Cu-5% (by weight) Mg alloy before treatment, after hydrogen absorption treatment and after hydrogen desorption treatment, respectively.

BEST MODES FOR CARRYING OUT THE INVENTION

[0013] The present invention provides a technology of refining crystal grains of an alloy whose main constituent(s) is (are) an element(s) weak in affinity for hydrogen by hydrogen treatment. This alloy crystal grain refining technology includes a crystal grain ultrarefining technology by which the diameter of refined crystal grains can amount to 10 nm to

1 μm, in some cases to 10 nm to 0.5 μm; it further includes alloy systems suited for such technology, namely (A) alloys comprising (1) an element(s) weak in affinity for hydrogen as a main constituent(s) and (2) an element strong in affinity for hydrogen as well as (B) alloys derived from the alloy systems (A) by the present hydrogen absorption/hydrogen desorption treatment and now consisting of refined crystal grains. The alloy crystal grain refining technology includes incorporating an element strong in affinity for hydrogen in an alloy whose main constituent(s) is(are) an element(s) weak in affinity for hydrogen while making the most of the characteristics of that alloy; namely, it includes selecting an appropriate level of such incorporation or selecting an appropriate metal species to be incorporated and also includes a technology of selecting the treatment conditions for the hydrogen absorption/hydrogen desorption treatment. In short, it includes all matters (techniques, methods, etc.) by or according to which the desired results can be obtained by subjecting an alloy whose main constituent(s) is(are) an element(s) weak in affinity for hydrogen to the alloy crystal grain refinement described herein.

[0014] While it is difficult to cause hydrogen to be absorbed in simple substance elements weak in affinity for hydrogen or alloys constituted of such an element(s) alone, addition of an amount not smaller than 0.1% by weight of an element strong in affinity for hydrogen thereto, for example, gives alloys capable of absorbing hydrogen. These alloys each generally forms one solid solution phase or a multi-phase metallographic structure comprising two or more phases including a solid solution. The present invention provides a technology of refining crystal grains of an alloy whose main constituent(s) is(are) an element(s) weak in affinity for hydrogen. When an alloy whose main constituent(s) is(are) an element(s) weak in affinity for hydrogen and which contains an element strong in affinity for hydrogen as a result of causing such element or phase strong in affinity for hydrogen to be present in an alloy whose main constituent(s) is(are) an element(s) weak in affinity for hydrogen is subjected to heat treatment involving hydrogen absorption and desorption, the crystal grains in the alloy can be ultrarefined and the alloy can be provided with ultrahigh strength. Thus, various properties of the alloy can be improved and ameliorated.

[0015] The element(s) weak in affinity for hydrogen can be selected from the group consisting of elements of the groups 6-10 of the periodic table of the elements (except for the element Pd), typically Cr, Mn, Fe, Co and Ni, and elements of the groups 11-15 of the periodic table of the elements, typically Cu, Ag, Au, Zn and Al. The alloy in question may contain only one species or two or more species of such alloy constituent elements weak in affinity for hydrogen.

[0016] As the elements of the groups 6-10 of the periodic table of the elements, there may be mentioned Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni and Pt, among others. As the elements of the groups 11-15 of the periodic table of the elements, there may be mentioned Cu, Ag, Au, Zn, Cd, Hg, Al, Ga, In, Tl, Ge, Sn, Pb, Sb and Bi, among others. Typically, from the viewpoint of utilization as structural metals, there may be mentioned alloys whose main constituent (s) is(are) selected from the group consisting of Cr, Mn, Fe, Co, Ni, Cu, Ag, Au, Zn and Al, among others. Thus, Cr-based alloys, Mn-based alloys, Fe-based alloys, Co-based alloys, Ni-based alloys, Cu-based alloys, Zn-based alloys, Al-based alloys, Ag-based alloys, Au-based alloys, Ni-Cr-based alloys, Ni-Co-based alloys, Cr-Mn-based alloys and Ni-Fe-based alloys, among others, may be included.

[0017] The element strong in affinity for hydrogen can be selected from the group consisting of alkali metals such as Li and Na, alkaline earth metals such as Mg and Ca, rare earth metals such as La and Ce, transition metals of the groups 3-5 of the periodic table of the elements, typically Ti and V, and Pd. The element strong in affinity for hydrogen and to be incorporated in such alloys as mentioned above for enabling application of the alloy crystal grain refining technology thereto may comprise one species or two or more species selected from the group mentioned above.

[0018] The alkali metal elements include Li, Na, K, Rb, Cs, etc. The alkaline earth metal elements include Mg, Ca, Sr, Ba, etc. The transition metals of the groups 3-5 of the periodic table of the elements include Sc, Y, Ti, Zr, Hf, V, Nb, Ta, rare earth metals, mischmetal and so forth. The rare earth metals include lanthanoids and actinoids, and the lanthanoids include La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu and the actinoids include Ac and Th, etc. Typically, the additive metal can be selected from those which will not adversely affect the base metal, and it can suitably selected from the low cost and/or high affinity for hydrogen viewpoint, among others. Preferably, it can be selected, for example, from the group consisting of Li, Na, Mg, Ca, La, Ce, mischmetal, Ti and V, among others.

[0019] The content of the element strong in affinity for hydrogen in the alloy systems to which the present invention is applicable may be not lower than 0.1% by weight as a total amount. In some cases, the content of the element strong in affinity for hydrogen may be 0.1-45% by weight; in other instances, it may be 0.1-35% by weight, or 0.1-25% by weight, typically 1-45% by weight or, in other cases, it may be 2-35% by weight, or 5-25% by weight or, further, 4-25% by weight; in other instances, it may be 5-20% by weight or 5-15% by weight, for instance. That amount can be properly determined at an appropriate level by carrying out experiments according to the disclosure in the present specification and it is also possible and preferable to vary the same according to the other party(ies) (element(s) weak in affinity for hydrogen) to be combined therewith.

[0020] The alloy to which the present invention is to be applied may contain at least one member selected from the group consisting of B, C, Si, N, P, As, O, S, Se, Te, F, C, B, I and Be in the periodic table of the elements provided that the intended or desired objects and effects or workings can be attained or produced. So long as alloys excellent in physical properties can be obtained by applying the present invention, the contents of these elements are not particularly restricted.

[0021] As already mentioned hereinabove, there are certain examples so far known in the art in which crystal grain refinement is attained by the hydrogen absorption/desorption method with alloys based on an element(s) strong in affinity for hydrogen or intermetallic compounds containing an element(s) strong in affinity for hydrogen abundantly, for example Nd-Fe-B type compound magnets, Ti-Al-V type alloys and Mg-Al type alloys. However, there is no specific example disclosed concerning application of the hydrogen absorption/desorption method to alloys based on an element(s) weak in affinity for hydrogen.

[0022] The present alloy crystal grain refining technology comprises a treatment for causing an alloy to absorb hydrogen. For causing the alloy to absorb hydrogen, the alloy is placed in a hydrogen atmosphere at a pressure of at least 1 atmosphere and the treatment is carried out within a temperature range of 0˚C to $0.8T_M$. The minimum temperature is defined by the value at which hydrogen absorption proceeds at a sufficient rate of reaction and, as for the maximum temperature, the treatment is desirably carried out within a temperature range not higher than the temperature at which the alloy phase associated with the element strong in affinity for hydrogen as contained in each alloy undergoes hydrogenation at the hydrogen pressure applied. A typical temperature range for the hydrogen absorption step is, for example, 10-800˚C, or 50-700˚C in some instances, or 100-600˚C or, further, 200-500˚C. It is of course possible to select an appropriate temperature range according to the composition of the alloy to be treated. A suitable temperature range for hydrogen absorption treatment is 200-450˚C, or 300-400˚C, for instance.

[0023] As for the hydrogen, the hydrogen absorption treatment can be carried out in a hydrogen atmosphere at a pressure of at least 1 atmosphere. The pressure, among others, of the hydrogen-containing atmosphere, however, can be selected at an appropriate level according to the element strong in affinity for hydrogen. For example, the following conditions can be employed and are sometimes preferred: a hydrogen atmosphere at 0.1-20 MPa, a hydrogen atmosphere at 0.1-10 MPa, a hydrogen atmosphere at 0.1-5 MPa, a hydrogen atmosphere at 0.1-1 MPa, a hydrogen atmosphere at 0.2-2 MPa, or a hydrogen atmosphere at 5-10 MPa.

[0024] As for the time required for this hydrogen absorption treatment, an appropriate time can be properly selected so long as the intended or desired objects and effects or workings can be attained or produced; thus, an appropriate time can be adequately selected according to the alloy system to be treated, and an appropriate time can be properly selected according to such other conditions as the hydrogen pressure and treatment temperature. The treatment time can also be decided taking economy and efficiency into consideration; thus, for example, it may be 0.1 hour to 1 month, 0.5 hour to 2 weeks or 1 hour to 1 week in some instances, 1 hour to 5 days or 1.5 hours to 5 days in preferred cases, or 10-120 hours or 15-100 hours or, further, 20-75 hours in typical examples.

[0025] It is desirable that, upon absorption of hydrogen by this alloy, a chemical reaction or reactions proceed so that the alloy phase associated with the element strong in affinity for hydrogen, partially or wholly, may form a hydride or hydrogen-containing solid solution phase.

[0026] This alloy crystal grain refining technology comprises a treatment for releasing hydrogen from the alloy that has absorbed hydrogen. For example, the alloy that has absorbed hydrogen is then placed under hydrogen pressure conditions lower than the thermodynamic equilibrium pressure, if possible lower than 1 atmosphere, and hydrogen desorption is allowed to proceed within a temperature range of 0˚C to $0.8T_M$. It is of course possible to cause hydrogen desorption within a temperature range of 200˚C to $0.8T_M$. As for the atmosphere, vacuum degassing, if possible, is preferred. It is also desirable to cause hydrogen desorption at a temperature as low as possible, taking the crystal grain growth into consideration.

[0027] It is desirable that the same phase(s) as appearing before the hydrogen absorption reaction be partly or wholly reconstructed in the alloy after the hydrogen absorption-desorption treatment carried out in the manner mentioned above.

[0028] As mentioned hereinabove, a hydride or hydrogen-containing solid solution phase is formed in the alloy upon hydrogen absorption and, after hydrogen desorption, the same phase(s) as appearing before the hydrogen absorption reaction is(are) partly or wholly reconstructed and the crystal grains are thereby reduced in size to 1 μm or smaller. By applying the present invention, it is possible to reduce the alloy crystal grain diameter to the submicron order, for example about 0.1-0.2 μm. In some instances, an alloy obtained by treatment according to the invention has a reduced crystal grain diameter of 10 nm to 1 μm. As the alloys obtained, there may be mentioned alloys having a reduced crystal grain diameter of 0.1-0.5 μm.

[0029] Al-Mg type alloys are now described as a typical example of the alloy systems to which the hydrogen absorption/desorption heat treatment according to the present invention is applicable. In these Al-Mg type alloys, the level of incorporation of Mg can be not higher than 10% by weight, for instance; in other cases, it may be about 3% by weight. Thus, the Mg content may be 0.1-10% by weight, typically 3-8% by weight and, in other cases, it may be 3-5% by weight or 2-4% by weight, for instance.

[0030] Similarly, in Fe-V type alloys, the level of incorporation of V may be not higher than 15% by weight, for instance; in other cases, it may be about 5% by weight. Thus, the content of V may be 0.1-15% by weight, typically 3-10% by weight; in other instances, it may be 4-10% by weight or 4-6% by weight, for instance.

[0031] In Cu-Mg type alloys, the level of incorporation of Mg may be not higher than 10% by weight, for instance; in other cases, it may be about 6% by weight. Thus, the level of addition of Mg may be 0.1-10% by weight, typically 3-8% by weight; in other cases, it may be 3-6% by weight or 4-5% by weight, for instance.

[0032] The alloy crystal grain refining technology of the invention makes it possible to reduce the crystal grain diameter of alloy materials so far difficult to reduce the crystal grain diameter thereof or render such materials very fine in crystal grain diameter; thus, it becomes possible to markedly improve or ameliorate the mechanical properties, electromagnetic properties, workability and hydrogen absorption/desorption characteristics thereof, among others. Further, the materials thus reduced in crystal grain diameter are expected to be useful as nanotechnology materials utilizing the fact of their being fine grained, or also as coating particles, catalyst particles, thin linear materials for electrodes, compounding ingredient materials and so forth utilizing the superfine crystal grains themselves. Further, the alloy crystal grain refining technology of the invention is expected to markedly improve or ameliorate the vicinity of the surface of alloy powders or alloys or thin linear objects made thereof with respect to such properties and characteristics as enumerated above.

[0033] The mechanical properties and workability of an alloy (material), so referred to herein, may refer to the mechanical responses of the alloy material and/or the degree of convenience and reliability in manufacturing products using the same and the aesthetic features of the products; thus, they include, for example the elastic limit, yield stress, tensile strength, elongation, reduction in area, hardness, value of impact energy, rate of creep, fatigue limit and so forth and may refer to the properties associated with the heat resistance, strength at elevated temperature, corrosion resistance, superhardness, resistance to brittle fracture, fatigue resistance, resistance to low temperature brittleness, superplasticity, weldability, weather resistance, press workability, designability, printability, finger print resistance or removability, lubricity, adhesiveness, wear resistance, durability, and properties associated with the reliability improvement of materials. The electromagnetic properties may include electric conductivity, resistance characteristics and magnetic characteristics, among others. The hydrogen absorption/desorption characteristics may include the rate of occlusion or release of hydrogen, hydrogen occlusion or release temperature, durability and so forth.

[0034] The "periodic table of the elements" so referred to herein refers to the one according to the system of notation as adopted on the occasion of the 1989 revision of the nomenclature of inorganic chemistry by the International Union of Pure and Applied Chemistry (IUPAC).

EXAMPLES

[0035] The following examples illustrate the invention specifically. These examples are, however, given to show certain specific modes of embodiment thereof only for the purpose of illustrating the present invention. These examples are by no means limitative or restrictive of the scope of the invention disclosed herein. It is to be understood that various modes of embodiment of the invention based on the ideas and concepts disclosed herein are possible.

[0036] All the examples were carried out or can be carried out using standard technologies or techniques, which are well known and conventional to those skilled in the art, unless otherwise described in detail.

[0037] Selecting Al as an element weak in affinity for hydrogen and Mg as an element strong in affinity for hydrogen, a powder of an Al-based alloy with a composition of Al-7.8% (by weight) Mg was prepared. The alloy powder obtained was subjected to hydrogen absorption treatment in a hydrogen atmosphere at 7.5 MPa within a temperature range of 250-450˚C for 72 hours. The results of measurements of a phase appearing in the thus-obtained alloy by powder X ray diffractometry are shown in Fig. 2. It was revealed that when the Al-7.8% (by weight) Mg alloy is exposed to a hydrogen atmosphere within a temperature range of 300-400˚C, an MgH_2 phase appears, the Mg in solid solution form is thus hydrogenated to give MgH_2 and the alloy is disproportionated into Al and MgH_2.

[0038] Then, hydrogen absorption treatment was carried out at 350˚C, at which hydrogenation proceeds, for 24-72 hours to find out an optimum time. The results of measurements of a phase appearing in the thus-obtained alloy by powder X ray diffractometry are shown in Fig. 3. From the changes in lattice constant of Al with the increase in time, it was revealed that the Mg content in the Al solid solution phase also changed. In particular, it can be estimated from the lattice constants of the Al alloy that the Mg content in the Al-7.8% (by weight) Mg alloy decreases by 24 hours or longer of treatment in hydrogen atmosphere (Table 1).

[Table 1]

Changes in Al lattice constant and Mg content in solid solution as functions of the hydrogen absorption treatment time		
	Lattice constant of Al (A)	Mg content in solid solution (% by weight)
Before hydrogenation	**4.0894**	**8.338**
After 24 hours of hydrogenation	**4.0615**	**2.663**
After 36 hours of hydrogenation	**4.0606**	**2.487**

(continued)

Changes in Al lattice constant and Mg content in solid solution as functions of the hydrogen absorption treatment time		
	Lattice constant of Al (A)	Mg content in solid solution (% by weight)
After 72 hours of hydrogenation	**4.0607**	**2.505**

[0039] Transmission electron-micrographs taken after 72 hours of hydrogen absorption treatment at 350˚C and 7.5 MPa are shown in Fig. 4. An MgO phase derived from MgH_2 is found finely dispersed, and this phase is considered to have been formed by oxidation of the MgH_2 phase during specimen preparation for electron microscopy. Therefore, MgH_2 is judged to have been finely dispersed in Al.

[0040] Following the hydrogen absorption treatment, the alloy was treated for hydrogen desorption therefrom by vacuum evacuation at 350˚C for 30 minutes to 5 hours. The results of measurements of a phase appearing in the thus-obtained alloy by powder X ray diffractometry are shown in Fig. 5. It was revealed that the same phase as appearing before hydrogen absorption is restored after 2 hours or longer.

[0041] Transmission electron-micrographs of the alloy after 4 hours of vacuum evacuation for hydrogen desorption treatment at 350˚C are shown in Fig. 6. It was revealed that the crystal grain diameter in the alloy texture obtained had been reduced to scores of nanometers.

[0042] While the example of the invention as given above is an example in which hydrogen was allowed to be occluded at 350˚C, followed by hydrogen release at 350˚C, the crystal grains can be rendered finer when the hydrogen desorption is carried out at a temperature as low as possible.

[0043] As an example demonstrating that even when the content of the element high in affinity for hydrogen is low, the invention is still effective, powder X ray diffraction patterns of Al-x% (by weight) Mg alloys (x = 3, 5, 7.8) differing in Mg content as recorded after hydrogen absorption treatment are shown in Fig. 7. The patterns indicate that a MgH_2 phase appeared in all the compositions and that the present treatment method is effective even when the Mg content in Al is as low as 3% by weight. Further, the X ray diffraction measurement results revealed that, upon the subsequent hydrogen-desorption heat-treatment, the alloy lattice constants return to the values before hydrogen treatment and, therefore, the element Mg once involved in hydride formation is redissolved to form a solid solution having the original alloy composition. It is seen that even when the Mg addition level is 3% by weight, the present invention is effective.

[0044] Selecting Fe as an element weak in affinity for hydrogen and V as an element strong in affinity for hydrogen, an Fe-based Fe-10% (by weight) V alloy was subjected to hydrogen absorption treatment in a hydrogen atmosphere at 7.5 MPa within a temperature range of 100-450˚C for 72 hours. The contents of V in the mother phase as calculated from the lattice constants determined by powder X ray diffractometry of the alloys obtained are shown in Fig. 8. It was revealed that when the Fe-10% (by weight) V alloy was exposed to the hydrogen atmosphere at 250˚C, the content of V in the mother phase markedly decreased as compared with the other treatment temperatures. This revealed that a phase containing V, which is larger in atomic radius than Fe, had precipitated abundantly from the Fe-10% (by weight) V alloy phase upon the hydrogen-absorption heat-treatment at 250˚C. A transmission electron-micrograph of the alloy obtained by the hydrogen absorption treatment is shown in Fig. 9. It became obvious that minute precipitates, about 10 nm in size, presenting a white contrast and containing V more abundantly than the mother phase were present.

[0045] The results of X ray diffractometry of the alloy before and after the hydrogen absorption treatment at 250˚C and after the subsequent hydrogen desorption treatment by forced degassing are shown in Fig. 10. It was revealed that while the lattice constant before treatment was 0.2876 nm, the lattice constant decreased upon heat absorption treatment as shown in Fig. 8 and, after the subsequent hydrogen desorption treatment, the original lattice constant of 0.2876 nm was restored. This is an example showing that the hydrogen absorption treatment results in precipitation of a phase containing the element V, which is strong in affinity for hydrogen, abundantly and, upon the subsequent hydrogen desorption treatment, this precipitate phase disappears and the original alloy composition can be restored.

[0046] As an example other than those alloys, Cu was selected as an element weak in affinity for hydrogen and Mg as an element strong in that affinity, and a Cu-based Cu-5% Mg alloy was subjected to X-ray diffractometry before treatment, after hydrogen absorption treatment and after hydrogen desorption treatment. The results are shown in Fig. 11. It is seen that, before treatment, the Cu-5% Mg phase alone was observed and, after hydrogen absorption treatment, a phase smaller in lattice constant than that phase newly appeared and, after the subsequent hydrogen desorption treatment, the original alloy phase was restored. Thus, for this alloy system, too, an example of the occurrence of the same phase change was obtained.

[0047] By carrying out the alloy crystal grain refining technology of the invention, it is possible to reduce the crystal grain diameter of aluminum alloys expected to serve as lightweight alloys for practical use to the submicron order, for example about 0.1-10 μm or further to about 0.05-1.0 μm. Further, by carrying out the alloy crystal grain refining technology of the invention, it is possible to reduce the crystal grain diameter of copper alloys expected as functional alloys for practical use to the submicron order, for example about 0.1-10 μm or, further to about 0.1-1.5 μm. Similarly, by carrying out the alloy crystal grain refining technology of the invention, it is possible to reduce the crystal grain diameter of iron-based alloys expected as steel materials to serve as various functional alloys or superalloys to the submicron order, for example about 0.01-5 μm or, further to about 0.01-0.2 μm.

[0048] According to the present invention, those alloy materials whose crystal grain refining has so far been difficult to achieve can now be subjected to crystal grain refining and, as a result, the mechanical properties, electromagnetic properties and workability, among others, can be markedly improved; thus, it can be expected that those materials which are promising but difficult to work and utilize so far will become effectively utilizable.

INDUSTRIAL APPLICABILITY

[0049] The development of novel materials from the viewpoint of weight reduction, high functionalization, ultrahigh strength, beautifulness and/or tough and feel, among others is now still earnestly demanded and, when such problems are solved by striving for reduction in alloy crystal grain diameter in those materials which are promising from such viewpoint but are difficult to produce and work, hence cannot be utilized or applied, the future of application of a wide variety of such alloy materials will become bright. The present invention makes it possible to improve the mechanical properties and workability, among others, of alloys whose main constituent(s) is(are) an element(s) weak in affinity for hydrogen and, therefore, use them in various fields of application.

[0050] It is evident that the present invention can be practiced in other ways than those illustrated hereinabove and in the examples, in particular. A number of alterations and modifications are possible in view of the teachings given hereinabove and they also fall within the scope of the claims attached hereto.

Claims

1. A method of refining crystal grains of an alloy whose main constituent(s) is(are) an element(s) weak in affinity for hydrogen and which contains an element strong in affinity for hydrogen which method is **characterized in that** the alloy is subjected to hydrogen absorption/desorption heat treatment involving causing the alloy to occlude hydrogen within a temperature range of 0˚C to $0.8T_M$ (T_M being the melting point of the metal or alloy as expressed in terms of absolute temperature) and then allowing the hydrogen to be released within a temperature range of 0˚C to $0.8T_M$.

2. A method of refining crystal grains of an alloy as set forth in Claim 1 which is **characterized in that** the alloy system to which the hydrogen absorption/desorption heat treatment is applicable is mainly an alloy comprising, as an element(s) weak in affinity for hydrogen, an element or a range of elements selected from elements of the groups 6-10 of the periodic table of the elements (except for Pd), typically Cr, Mn, Fe, Co and Ni, and elements of the groups 11-15 of the periodic table of the elements, typically Cu, Ag, Au, Zn and Al.

3. A method of refining crystal grains of an alloy as set forth in Claim 1 or 2 which is **characterized in that** the alloy system to which the hydrogen absorption/desorption heat treatment is applicable contains at least one metal strong in affinity for hydrogen as selected from the group consisting of alkali metals such as Li and Na, alkaline earth metals such as Mg and Ca, rare earth metals such as La and Ce, transition metals of the groups 3-5 of the periodic table of the elements, typically Ti and V, and Pd.

4. A crystal grain refined alloy **characterized in that** it is an alloy whose main constituent(s) is(are) an element(s) weak in affinity for hydrogen and which contains an element strong in affinity for hydrogen and is obtained by subjecting said alloy to hydrogen absorption/desorption heat treatment involving causing the alloy to occlude hydrogen within a temperature range of 0˚C to $0.8T_M$ (T_M being the melting point of the metal or alloy as expressed in terms of absolute temperature) and then allowing the hydrogen to be released within a temperature range of 0˚C to $0.8T_M$, said alloy consisting of alloy crystal grains refined by said heat treatment.

5. An alloy as set forth in Claim 4 **characterized in that** the alloy system to which the hydrogen absorption/desorption heat treatment is applicable is mainly an alloy comprising, as an element(s) weak in affinity for hydrogen, an element or a range of elements selected from elements of the groups 6-10 of the periodic table of the elements (except for Pd), typically Cr, Mn, Fe, Co and Ni, and elements of the groups 11-15 of the periodic table of the elements, typically Cu, Ag, Au, Zn and Al.

6. An alloy as set forth in Claim 4 or 5 **characterized in that** the alloy system to which the hydrogen absorption/desorption heat treatment is applicable contains at least one metal strong in affinity for hydrogen as selected from

the group consisting of alkali metals such as Li and Na, alkaline earth metals such as Mg and Ca, rare earth metals such as La and Ce, transition metals of the groups 3-5 of the periodic table of the elements, typically Ti and V, and Pd.

7. An alloy as set forth in any of Claims 4-6 **characterized in that** the refined crystal grain diameter is 10 nm to 10 μm.

Fig.01

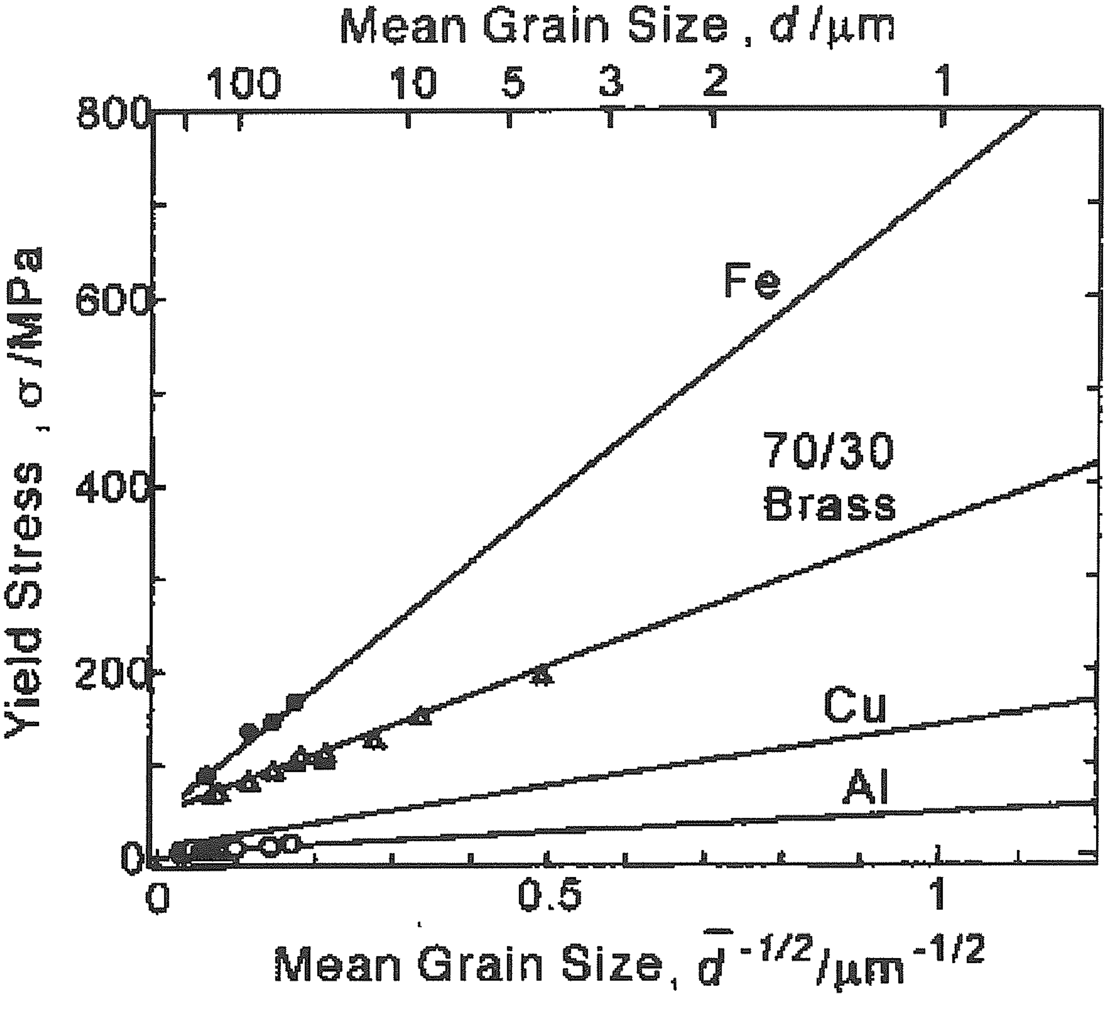

Mean Grain Size , $\bar{d}$ /μm
100
10
5
3
2
1
800
600
400
200
0
Yield Stress , σ /MPa
Fe
70/30
Brass
Cu
Al
0
0.5
1
Mean Grain Size, $\bar{d}^{-1/2}$/μm$^{-1/2}$

Fig.02

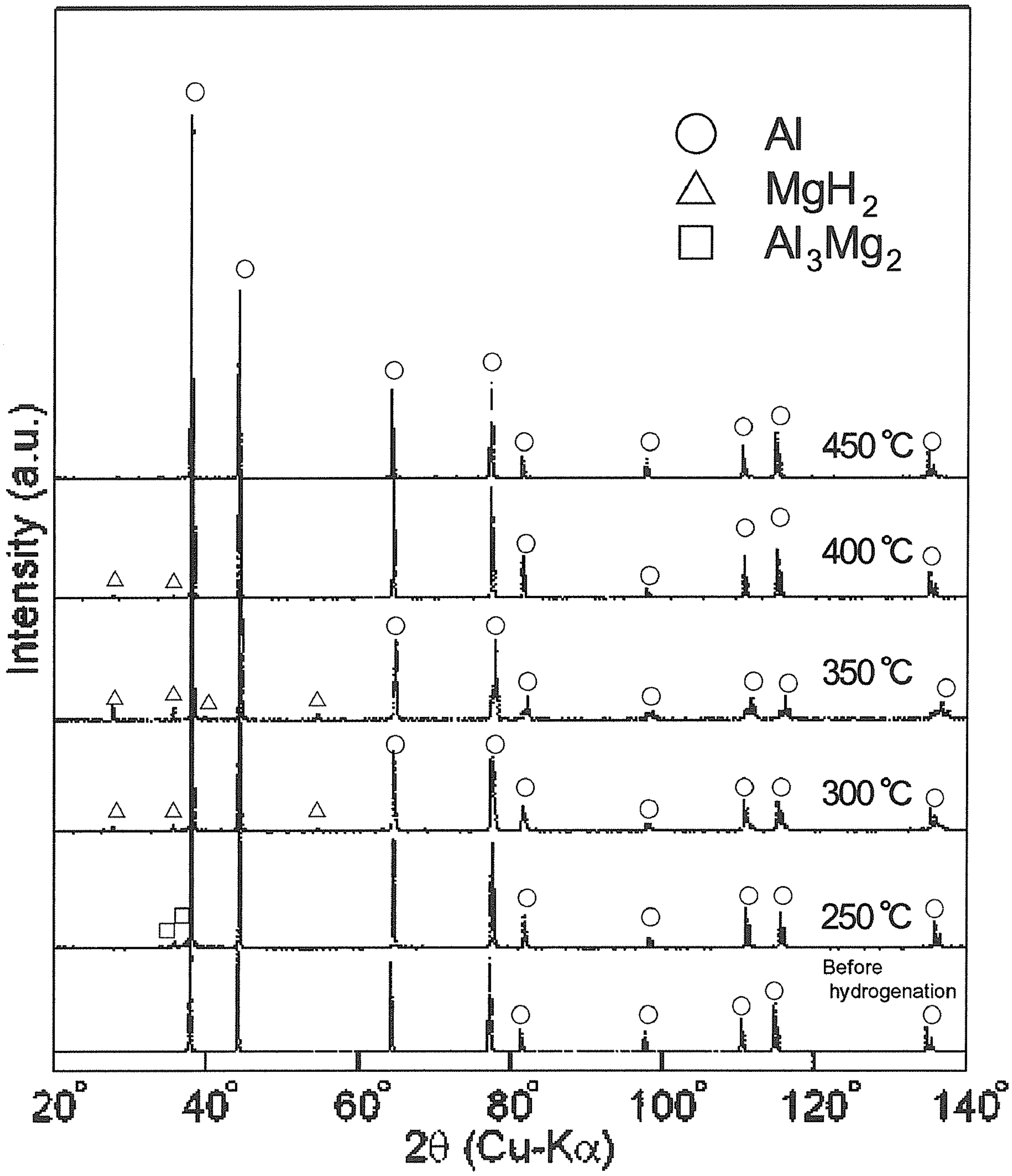

○ Al
△ MgH2
□ Al3Mg2
450 ℃
400 ℃
350 ℃
300 ℃
250 ℃
Before hydrogenation
Intensity (a.u.)
20°
40°
60°
80°
100°
120°
140°
2θ (Cu-Kα)

Fig.03

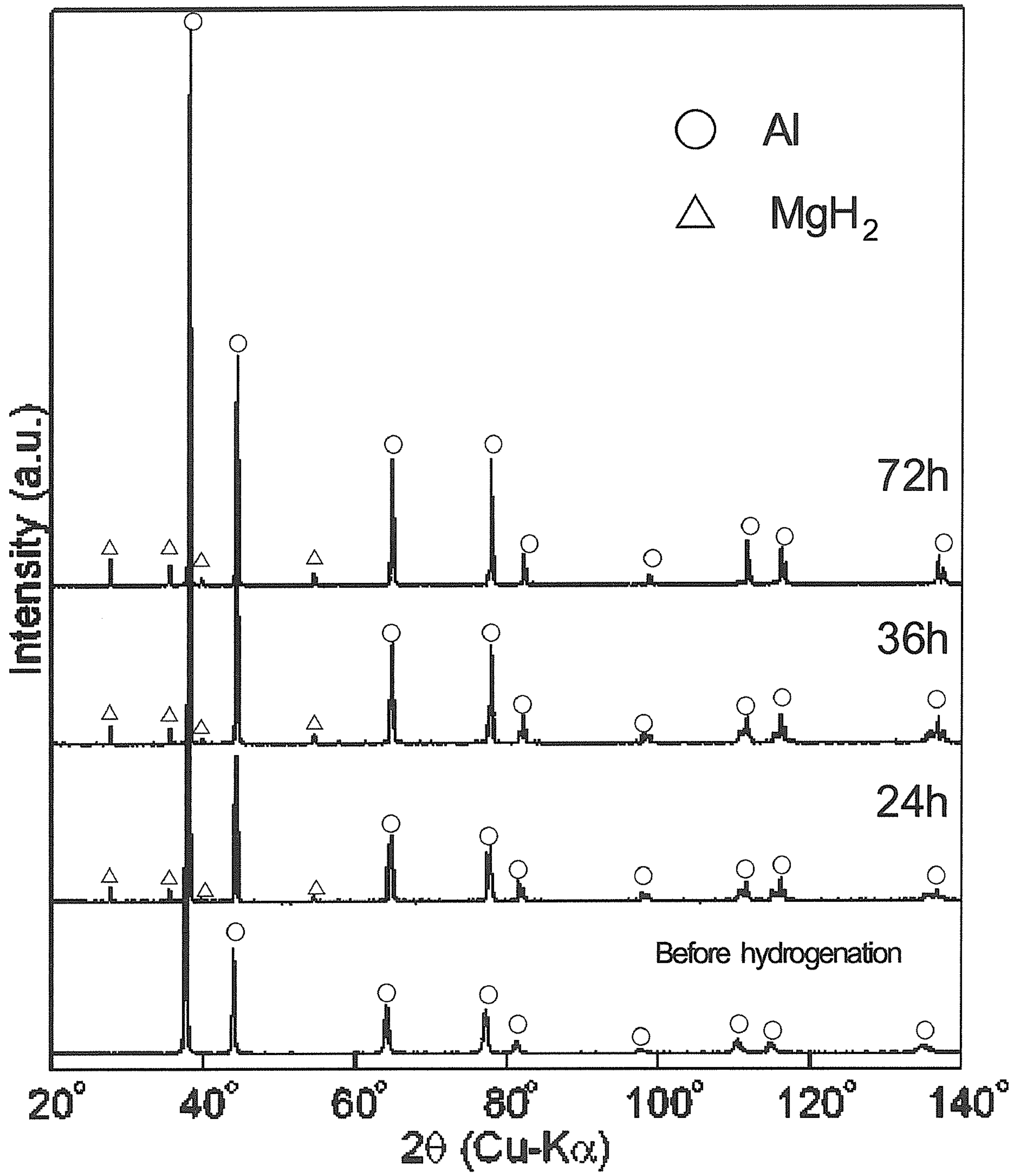

○ Al
△ MgH_2
72h
36h
24h
Before hydrogenation
Intensity (a.u.)
20°
40°
60°
80°
100°
120°
140°
2θ (Cu-Kα)

Fig.04

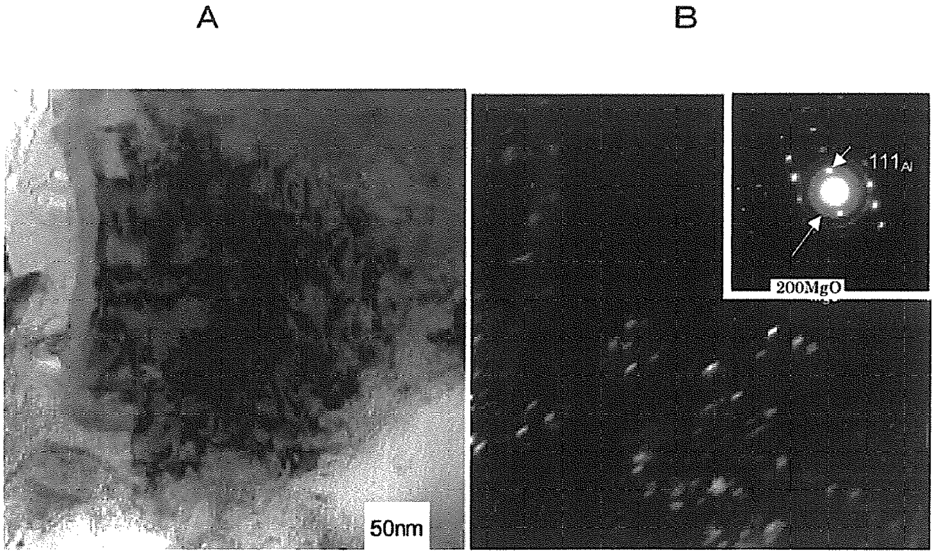


Fig.05

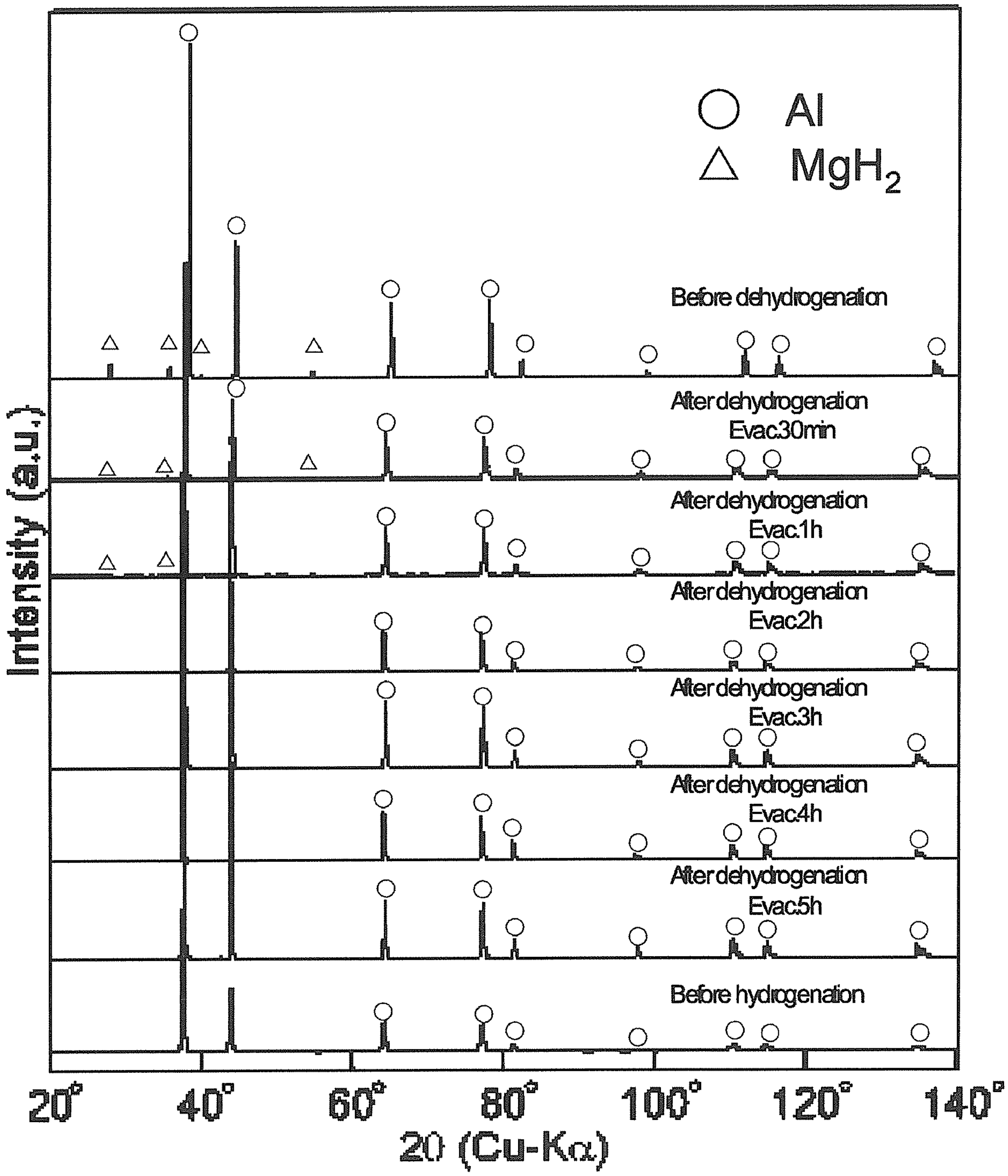

○ Al
△ MgH2
Before dehydrogenation
After dehydrogenation Evac.30min
After dehydrogenation Evac.1h
After dehydrogenation Evac.2h
After dehydrogenation Evac.3h
After dehydrogenation Evac.4h
After dehydrogenation Evac.5h
Before hydrogenation
Intensity (a.u.)
20°
40°
60°
80°
100°
120°
140°
2θ (Cu-Kα)

Fig.06

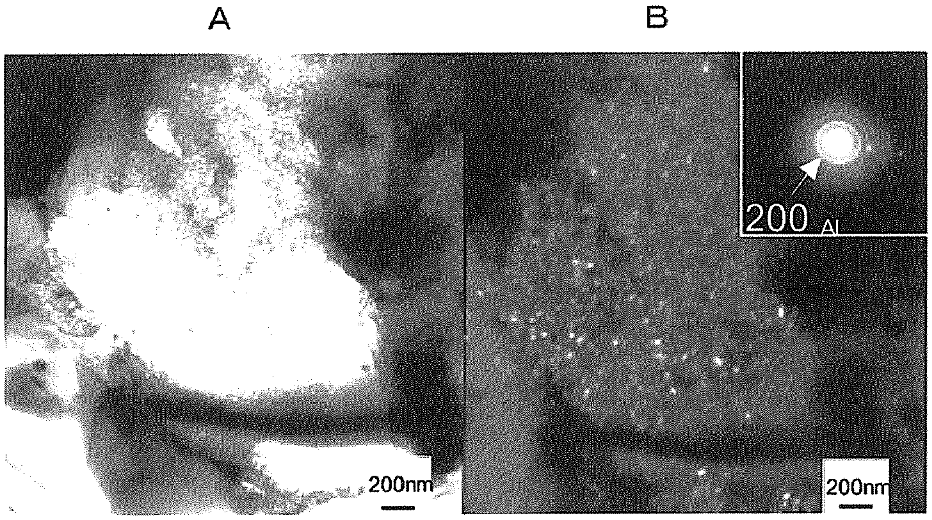


Fig.07

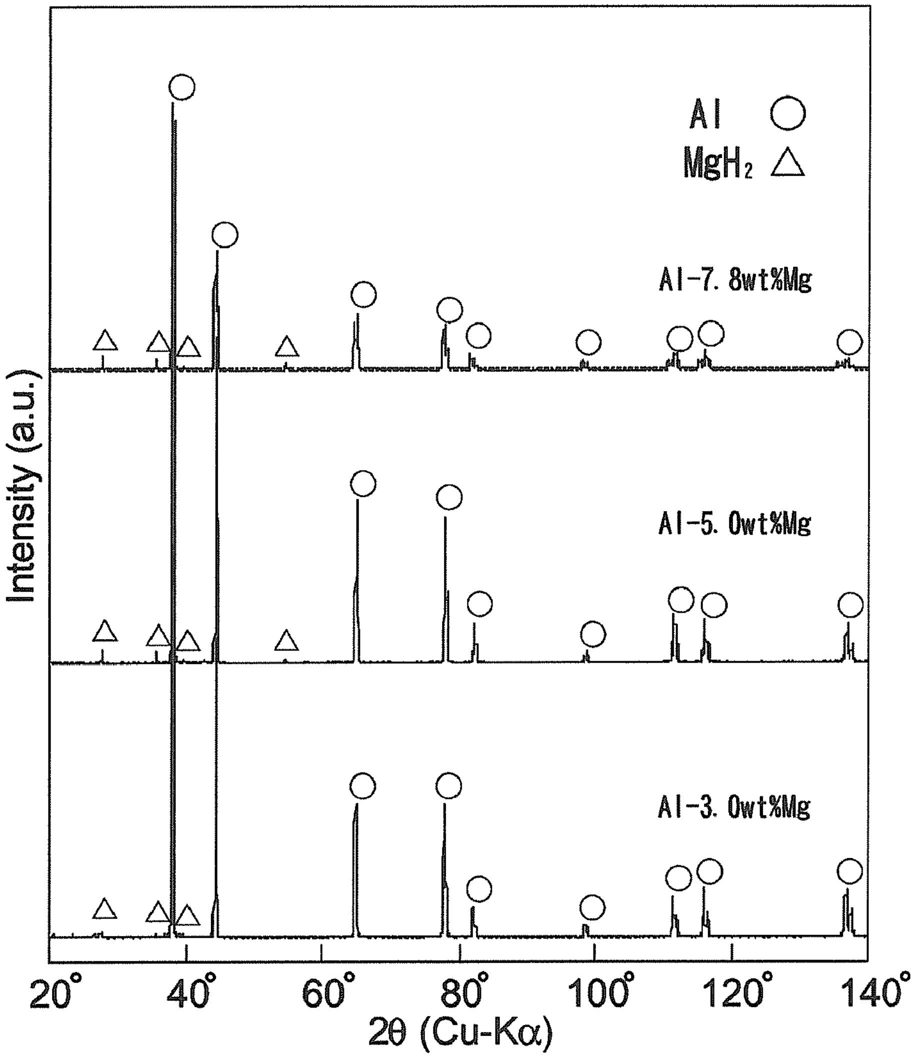

Al ○
MgH₂ △
Al-7.8wt%Mg
Al-5.0wt%Mg
Al-3.0wt%Mg
Intensity (a.u.)
20°
40°
60°
80°
100°
120°
140°
2θ (Cu-Kα)

Fig.08

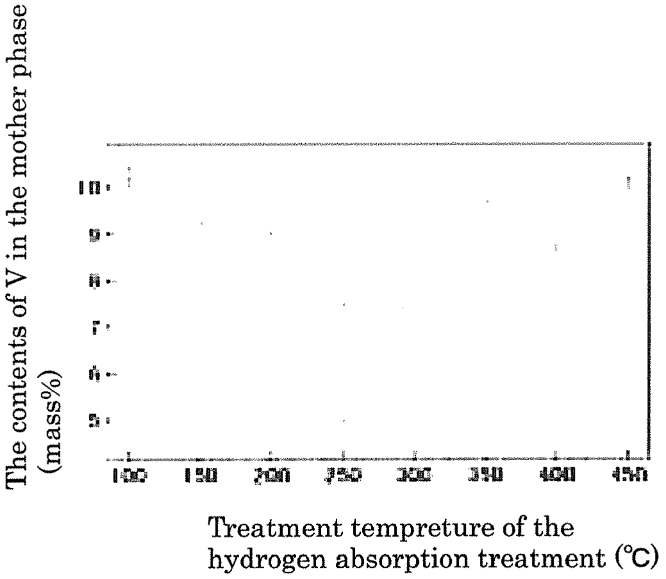

The contents of V in the mother phase (mass%)
10
9
8
7
6
5
100
150
200
250
300
350
400
450
Treatment tempreture of the hydrogen absorption treatment (℃)

Fig.09

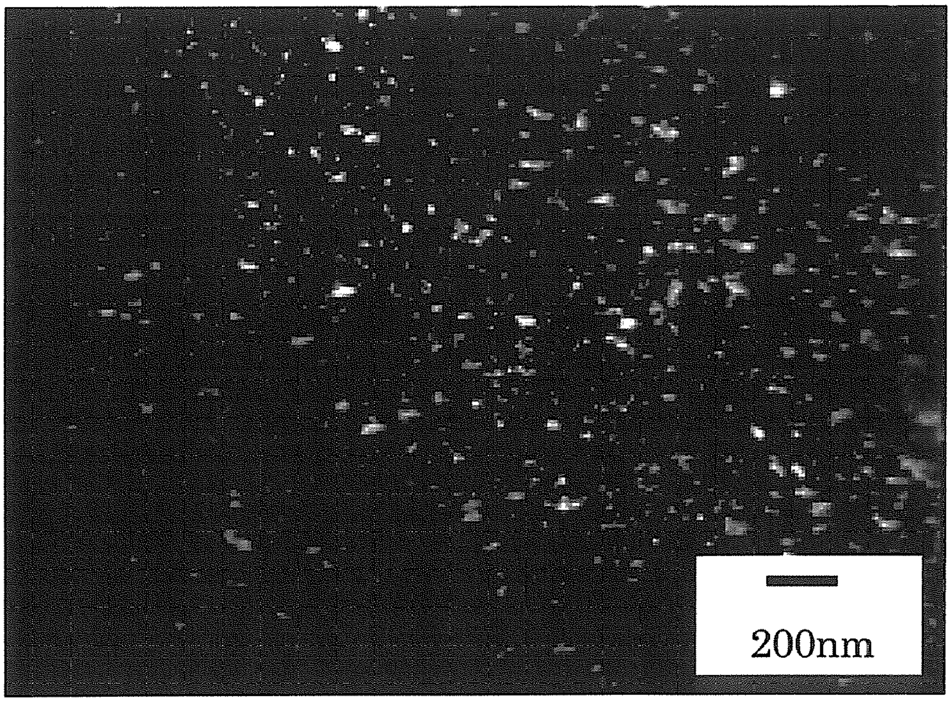


Fig.10

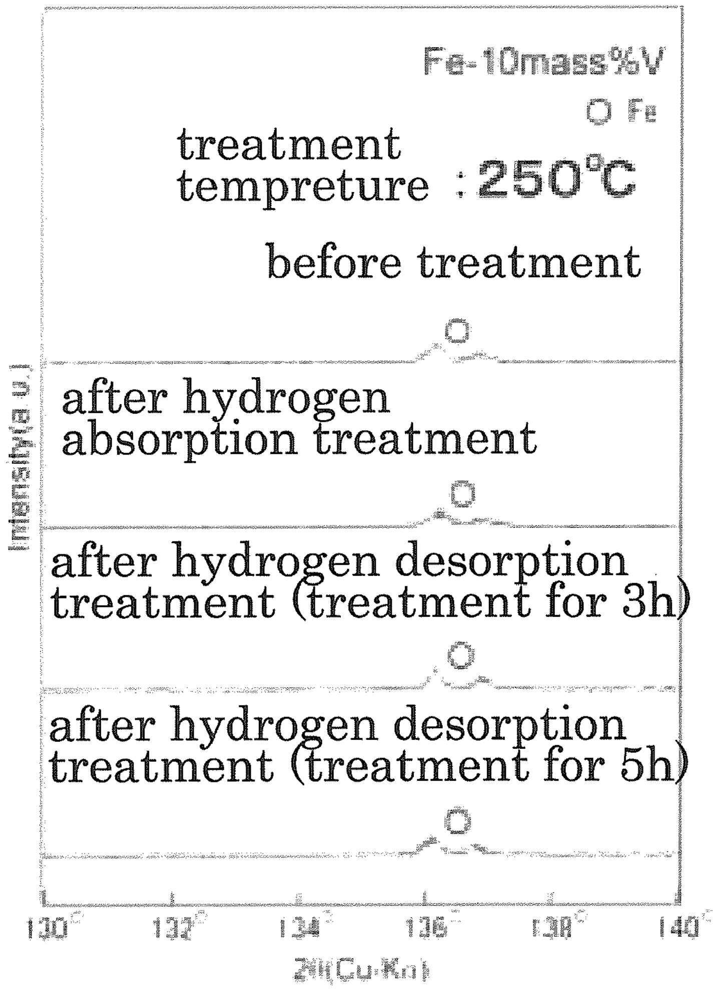
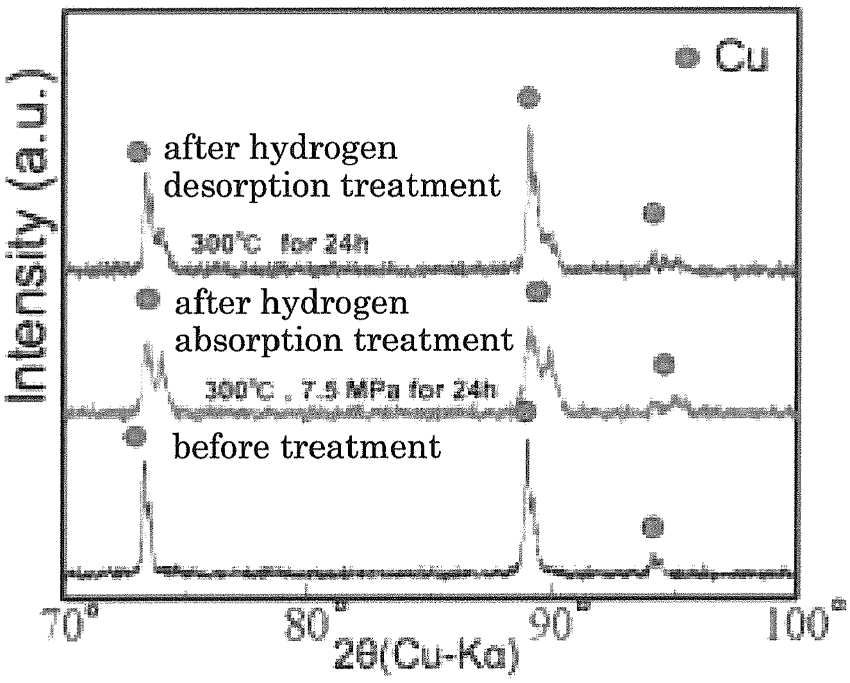

Fe-10mass%V
○ Fe
treatment tempreture : 250°C
before treatment
after hydrogen absorption treatment
after hydrogen desorption treatment (treatment for 3h)
after hydrogen desorption treatment (treatment for 5h)
Intensity(a.u.)
130°
132°
134°
136°
138°
140°
2θ(Cu-Kα)

Fig.11


● Cu
after hydrogen desorption treatment
300°C for 24h
after hydrogen absorption treatment
300°C, 7.5 MPa for 24h
before treatment
Intensity (a.u.)
70°
80°
90°
100°
2θ(Cu-Kα)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2005/005587

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl^7 C22F1/047, B22F1/00, C22C21/06, C22F1/02

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)
Int.Cl^7 C22F1/047, B22F1/00, C22C21/06, C22F1/02

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	1996-2005
Kokai Jitsuyo Shinan Koho	1971-2005	Toroku Jitsuyo Shinan Koho	1994-2005

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 11-80801 A (Sanyo Electric Co., Ltd.), 26 March, 1999 (26.03.99), Full text (Family: none)	1-7
X	JP 2002-118010 A (Toshiba Corp.), 19 April, 2002 (19.04.02), Full text & US 6416593 B2	1-7
X	JP 2003-193208 A (Toshiba Corp.), 09 July, 2003 (09.07.03), Full text (Family: none)	1-7

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

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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
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"X" 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
"Y" document of particular relevance; the claimed invention cannot be 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
"&" document member of the same patent family

Date of the actual completion of the international search 14 June, 2005 (14.06.05)	Date of mailing of the international search report 28 June, 2005 (28.06.05)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (January 2004)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2005/005587

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 2002-180174 A (Japan Metals & Chemicals Co., Ltd.), 26 June, 2002 (26.06.02), Par. No. [0011] (Family: none)	1-7
A	JP 2001-131723 A (Daido Steel Co., Ltd.), 15 May, 2001 (15.05.01), Full text (Family: none)	1-7

Form PCT/ISA/210 (continuation of second sheet) (January 2004)