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A request for correction of the abstract after aluminium-base matrix insert ultra. and cancel ultra before fine TiB-base particles dispersed has been filed pursuant to Rule 88 EPC. A decision on the request will be taken during the proceedings before the Examining Division (Guidelines for Examination in the EPO, A-V, 3.).

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(71) Applicant: **HONDA GIKEN KOGYO KABUSHIKI KAISHA**  
**1-1, Minami-Aoyama 2-chome**  
**Minato-ku**  
**Tokyo 107 (JP)**

(72) Inventor: **Takahashi, Kazuya, c/o Kabushiki Kaisha Honda**  
**Gijutsu Kenkyujo,**  
**4-1, Chuo 1-chome**  
**Wako-shi,**  
**Saitama-ken (JP)**  
Inventor: **Shinohara, Masashi, c/o Kabushiki Kaisha Honda**  
**Gijutsu Kenkyujo,**  
**4-1, Chuo 1-chome**  
**Wako-shi,**  
**Saitama-ken (JP)**

(74) Representative: **Fincke, Karl Theodor,**  
**Dipl.-Phys. Dr. et al**  
**Patentanwälte**  
**H. Weickmann, Dr. K. Fincke**  
**F.A. Weickmann, B. Huber**  
**Dr. H. Liska, Dr. J. Prechtel, Dr. B. Böhm**  
**Postfach 86 08 20**  
**D-81635 München (DE)**

(54) **High-strength aluminum alloy and method of manufacturing same**

(57) A high-strength aluminum alloy has an aluminum-base matrix, ultra-fine TiB-base particles dispersed in the aluminum-base matrix and having a maximum particle diameter of 50nm, and fine TiB-base particles dispersed in the aluminum-base matrix and having a maximum particle diameter of 1.2  $\mu$ m. The aluminum-base matrix is composed of Al and Ti, the fine TiB-base particles are composed of Ti and B and free of Fe or Fe and Si, and the ultra-fine TiB-base particles are composed of Ti and B and contain Fe or Fe and Si.

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The present invention relates to a high-strength aluminum alloy and a method of manufacturing such a high-strength aluminum alloy, and more particularly to a high-strength aluminum alloy which comprises thermally stable particles of titanium boride (TiB) that are dispersed in an aluminum-base matrix, and a method of manufacturing such a high-strength aluminum alloy.

There has heretofore been known an aluminum alloy produced by adding a titanium-containing compound and a boron-containing compound to a molten aluminum alloy, thereby generating TiB-base particles dispersed in the molten aluminum alloy. For details, reference should be made to Japanese laid-open patent publication No. 63-140059.

In order to increase the strength of an aluminum alloy with TiB-base particles, it is most important to disperse fine TiB-base particles in an aluminum matrix. It has been customary to employ TiB-base particles having an average diameter ranging from about 0.4 to 0.8  $\mu\text{m}$ . It has been difficult to reduce the size of TiB-base particles to smaller diameters due to limitations that have heretofore been imposed on the diameter control of TiB-base particles.

Japanese laid-open patent publication No. 48-84013 discloses an alloy of aluminum, titanium, and boron.

U.S. Patent No. 4,726,842 reveals metallic materials reinforced by a continuous network of a ceramic phase.

U.S. Patent No. 5,100,618 discloses a method of producing an aluminum grain refiner such as aluminum - titanium - boron grain refiner.

Japanese patent disclosure No. 6-502692 shows a method of manufacturing an aluminum matrix containing dispersed ceramic boride particles.

It is therefore an object of the present invention to provide a high-strength aluminum alloy which is composed of ultra-fine TiB-base particles containing a certain alloying element or elements, and a method of manufacturing such a high-strength aluminum alloy.

According to the present invention, there is provided a high-strength aluminum alloy comprising an aluminum-base matrix, and TiB-base particles dispersed in the aluminum-base alloy and containing either Fe or Fe and Si.

In the high-strength aluminum alloy, a ratio  $(f + s)/t$  is in the range of  $0.001 \leq (f + s)/t \leq 0.3$  where  $f$  represents the amount of Fe expressed by a gram atomic weight,  $s$  represents the amount of Si expressed by a gram atomic weight (including  $s = 0$ ), and  $t$  represents the amount of Ti expressed by a gram atomic weight.

The TiB-base particles have a particle diameter  $d$  in the range of  $d \leq 50 \text{ nm}$ .

The aluminum-base matrix is made of Al and Ti.

According to the present invention, there is also provided a high-strength aluminum alloy comprising an aluminum-base matrix, ultra-fine TiB-base particles dispersed in the aluminum-base matrix and having a maximum particle diameter of 50 nm, and fine TiB-base particles dispersed in the aluminum-base matrix and having a maximum particle diameter of 1.2  $\mu\text{m}$ . The aluminum-base matrix is composed of Al and Ti.

The ultra-fine TiB-base particles are composed of Ti and B and contain Fe or Fe and Si.

The fine TiB-base particles are composed of Ti and B and free of Fe or Fe and Si.

According to the present invention, there is further provided a method of manufacturing a high-strength aluminum alloy, comprising the steps of preparing a molten aluminum alloy containing Fe, and adding at least one of Ti and a Ti-containing compound and at least one of B and B-containing compound to the molten aluminum alloy, thus producing TiB-base particles containing Fe.

In the method, a ratio  $f/t$  is in the range of  $0.001 \leq f/t \leq 0.3$  where  $f$  represents the amount of Fe expressed by a gram atomic weight, and  $t$  represents the amount of Ti expressed by a gram atomic weight.

According to the present invention, there is further provided a method of manufacturing a high-strength aluminum alloy, comprising the steps of preparing a molten aluminum alloy containing Fe and Si, and adding at least one of Ti and a Ti-containing compound and at least one of B and B-containing compound to the molten aluminum alloy, thus producing either both TiB-base particles containing Fe and TiB-base particles containing Fe and Si, or TiB-base particles containing Fe and Si.

In the method, a ratio  $(f + s)/t$  is in the range of  $0.001 \leq (f + s)/t \leq 0.3$  where  $f$  represents the amount of Fe expressed by a gram atomic weight,  $s$  represents the amount of Si expressed by a gram atomic weight (including  $s = 0$ ), and  $t$  represents the amount of Ti expressed by a gram atomic weight.

The Ti-containing compound comprises  $\text{K}_2\text{TiF}_6$  and the B-containing compound comprises  $\text{KBF}_4$ .

Since the TiB-base particles have a particle diameter  $d$  in the range of  $d \leq 50 \text{ nm}$ , they are ultra-fine particles which are effective in increasing the strength of the aluminum alloy.

Each of the above methods allows the aluminum alloy to be manufactured with ease, and hence can mass-produce high-strength aluminum alloys.

The above and other objects, features, and advantages of the present invention will become apparent from the following description when taken in conjunction with the accompanying drawings which illustrate preferred embodiments of the present invention by way of example.

FIG. 1 is a schematic diagram showing a metallic structure of a high-strength aluminum alloy according to the present invention;

FIG. 2 is a microscopic representation of the metallic structure of the high-strength aluminum alloy;

FIG. 3 is a schematic diagram of the metallic structure shown in FIG. 2;

FIG. 4 is a graph showing the result of an elemental analysis conducted on an aluminum-base matrix by energy dispersive X-ray spectroscopy (EDX);

FIG. 5 is a graph showing the result of an elemental analysis conducted on an ultra-fine TiB-base particle by EDX;

FIG. 6 is a graph showing the result of an elemental analysis conducted on another ultra-fine TiB-base particle by EDX;

FIG. 7 is a graph showing the result of an elemental analysis conducted on a fine TiB-base particle by EDX;

FIG. 8 is a graph showing the 0.2 %-offset yield strengths of an aluminum alloy I according to Inventive Example 1 and an aluminum alloy I according to Comparative Example 1;

FIG. 9 is a graph showing the 0.2 %-offset yield strengths of an aluminum alloy II according to Inventive Example 2 and an aluminum alloy II according to Comparative Example 2; and

FIG. 10 is a graph showing the 0.2 %-offset yield strengths of an aluminum alloy III according to Inventive Example 3 and an aluminum alloy III according to Comparative Example 3.

FIG. 1 shows a metallic structure of a high-strength aluminum alloy according to the present invention. As shown in FIG. 1, the high-strength aluminum alloy has an aluminum-base matrix 1 in which there are dispersed ultra-fine TiB-base particles 2 having sizes on the order of nanometers (nm) and fine TiB-base particles 3 having sizes on the order of micrometers ( $\mu\text{m}$ ). The ultra-fine TiB-base particles 2, which may, for example, be titanium diboride ( $\text{TiB}_2$ ) particles containing iron (Fe) or Fe and silicon (Si), have a maximum particle diameter of 50 nm and an average particle diameter of 20 nm. Therefore, the ultra-fine TiB-base particles 2 have particle diameters "d" in the range of  $d \leq 50$  nm. The fine TiB-base particles 3, which also may, for example, be  $\text{TiB}_2$  particles free of, i.e., not containing, Fe or Fe and Si, have a maximum particle diameter of  $1.2 \mu\text{m}$  and an average particle diameter in the range of from 0.4 to

$0.8 \mu\text{m}$ . Therefore, the fine TiB-base particles 3 have particle diameters "d" in the range of  $d \leq 1.2 \mu\text{m}$ .

The TiB-base particles 2 are ultra-fine particles because they contain Fe or Fe and Si. The ultra-fine TiB-base particles 2 that are dispersed in the aluminum-base matrix 1 are effective to increase the 0.2 %-offset yield strength  $\sigma_{0.2}$  of the aluminum-base matrix 1 one and a half (1.5) times that of an aluminum-base matrix in which only TiB-base particles 3 were dispersed.

There is a certain correlation between the amounts of Fe, Si, and Ti contained in the high-strength aluminum alloy which contains the ultra-fine TiB-base particles 2. Specifically, if it is assumed that the amount of Fe expressed by a gram atomic weight is represented by "f", the amount of Si expressed by a gram atomic weight is represented by "s" (including  $s = 0$ ), and the amount of Ti expressed by a gram atomic weight is represented by "t", then the ratio  $(f + s)/t$  is in the range of  $0.001 \leq (f + s)/t \leq 0.3$ . If the ratio  $(f + s)/t$  were smaller than 0.001, then the average particle diameter of the TiB-base particles 2 would be equal to the average particle diameter of the fine TiB-base particles 3, and hence would not be ultra-fine particles. If the ratio  $(f + s)/t$  were greater than 0.3, then the amounts of Fe and Si would be excessive enough to produce bodies of a coarse intermetallic compound such as  $\text{Al}_3\text{Fe}$ , lowering the characteristics of the aluminum alloy.

It is preferable that the ratio  $(f + s)/t$  be in the range of  $0.001 < (f + s)/t \leq 0.3$ , and also that the volume fraction  $V_f$  of the TiB-base particles 2, 3 in the aluminum-base matrix 1 be in the range of  $V_f \geq 5 \%$ , and the volume fraction  $V_f$  of the ultra-fine TiB-base particles 2 be in the range of  $V_f \geq 1 \%$ . The volume fraction  $V_f$  of the ultra-fine TiB-base particles 2 is greater as the ratio  $(f + s)/t$  approaches the value "0.3". The particles dispersed in the aluminum-base matrix 1 may be composed of only ultra-fine TiB-base particles 2.

The aluminum alloy composed of the ultra-fine TiB-base particles 2 (and the fine TiB-base particles 3) dispersed in the aluminum-base matrix 1 can be manufactured by either preparing a molten aluminum alloy containing Fe in an inert atmosphere and then adding at least one of Ti and a Ti-containing compound and at least one of B and B-containing compound to the molten aluminum alloy, thus producing ultra-fine TiB-base particles 2 (and fine TiB-base particles 3) containing Fe, or preparing a molten aluminum alloy containing Fe and Si in an inert atmosphere and then adding at least one of Ti and a Ti-containing compound and at least one of B and B-containing compound to the molten aluminum alloy, thus producing either both ultra-fine TiB-base particles 2 containing Fe

and ultra-fine TiB-base particles 2 containing Fe and Si, or ultra-fine TiB-base particles 2 containing Fe and Si.

The amounts of Fe, Si, and Ti contained in the aluminum alloy thus manufactured are correlated such that the ratio  $(f + s)/t$  is in the range of  $0.001 \leq (f + s)/t \leq 0.3$  (including  $s = 0$ ).

Ti and B are added as powders. The Ti-containing compound may be a powder of  $K_2TiF_6$  - (potassium titanium fluoride), and the B-containing compound may be a powder of  $KBF_4$  (potassium boron fluoride). The  $K_2TiF_6$  and  $KBF_4$  function as a flux and can be dissolved even when the temperature of the molten aluminum alloy is low. Therefore, they are effective to reduce the diameter of the fine TiB-base particles 3 for increasing the strength of the aluminum alloy.

The amounts of Ti and B which are added are in the ranges  $5.87 \text{ g} \leq \text{Ti} \leq 260 \text{ g}$  and  $2.65 \text{ g} \leq \text{B} \leq 117.5 \text{ g}$ , respectively, with respect to 100 g of molten aluminum alloy. If  $\text{Ti} < 5.87 \text{ g}$  and  $\text{B} < 2.65 \text{ g}$ , then it would be difficult to generate TiB-base particles. If  $\text{Ti} > 260 \text{ g}$  and  $\text{B} > 117.5 \text{ g}$ , then the ingot which is cast would crack.

The cast ingot is subsequently subjected to hot extrusion, if necessary, to remove shrinkage cavities.

Examples of the present invention will now be described below.

#### [Inventive Example 1]

(a) Using a crucible, a molten aluminum alloy composed of 0.17 g of Fe, 0.17 g of Si, and 380 g of Al was prepared at  $700^\circ\text{C}$  in an argon (Ar) gas atmosphere.

(b) To the molten aluminum alloy, there were simultaneously added 480 g of  $K_2TiF_6$  powder having a particle diameter of  $500 \mu\text{m}$  or less and 504 g of  $KBF_4$  powder having a particle diameter of  $500 \mu\text{m}$  or less. Then, the molten aluminum alloy was stirred using a stirring rod. The ratio  $(f + s)/t$  was 0.004. After confirming the end of a temperature rise of the molten aluminum alloy due to a chemical reaction, the molten aluminum alloy was left so as to be solidified in the crucible, and cooled into an ingot made of an aluminum alloy I.

(c) The ingot was taken out of the crucible, and extruded in a hot extrusion process at a temperature of  $500^\circ\text{C}$  with an extrusion ratio of 11, thereby producing an extruded round rod having a diameter of 9 mm.

(d) A specimen was produced from the extruded round rod, and its metallic structure was observed using a transmission electron microscope (TEM). As a result, it was confirmed, as shown in FIGS. 2 and 3, that countless ultra-fine

TiB-base particles 2 ( $2_1$ ,  $2_2$ ) and countless fine TiB-base particles 3 ( $3_1$ ) were dispersed in an aluminum-base matrix 1. The ultra-fine TiB-base particles 2 had a maximum particle diameter of 50 nm and an average particle diameter of 20 nm, and the fine TiB-base particles 3 had a maximum particle diameter of  $1.2 \mu\text{m}$  and an average-particle diameter of  $0.4 \mu\text{m}$ .

The specimen was subjected to elemental analyses by energy dispersive X-ray spectroscopy (EDX). The results of the elemental analyses are shown in FIGS. 4 through 7.

FIG. 4 shows the results of the elemental analysis of the aluminum-base matrix 1, and indicates that the aluminum-base matrix 1 is composed of Al and Ti.

FIG. 5 shows the results of the elemental analysis of one  $2_1$  of the ultra-fine TiB-base particles 2 shown in FIGS. 2 and 3. It can be seen from FIG. 5 that the ultra-fine TiB-base particle  $2_1$  is composed of Ti and B and contains Fe and Si. The peak indicated by Al in FIG. 5 represents a measurement error.

FIG. 6 shows the results of the elemental analysis of another one  $2_2$  of the ultra-fine TiB-base particles 2 shown in FIGS. 2 and 3. It can be seen from FIG. 6 that the ultra-fine TiB-base particle  $2_2$  is composed of Ti and B and contains Fe and Si. The peak indicated by Al in FIG. 6 represents a measurement error.

FIG. 7 shows the results of the elemental analysis of one  $3_1$  of the fine TiB-base particles 3 shown in FIGS. 2 and 3. It can be seen from FIG. 7 that the fine TiB-base particle  $3_1$  is composed of Ti and B and does not contain Fe and Si. The peak indicated by Al in FIG. 5 represents a measurement error.

(e) The extruded round rod was machined into a sample for use in a tensile test JIS (Japanese Industrial Standards) 14A. The sample had a gage length  $L$  of 22 mm and a diameter  $D$  of 4.0 mm. The tensile test conducted on the sample indicated that the sample had a 0.2 %-offset yield strength  $\sigma_{0.2}$  of 644 MPa.

#### [Comparative Example 1]

An aluminum alloy I according to Comparative Example 1 was manufactured and its characteristics were inspected as follows:

(a) Using a crucible, 380 g of molten aluminum composed of pure aluminum having a purity of 99.99 % was prepared at  $700^\circ\text{C}$  in an Ar gas atmosphere.

(b) To the molten aluminum, there were simultaneously added 480 g of  $K_2TiF_6$  powder having a particle diameter of  $500 \mu\text{m}$  or less and 504 g of  $KBF_4$  powder having a particle diameter of 500

$\mu\text{m}$  or less. Then, the molten aluminum was stirred using a stirring rod. The ratio  $(f + s)/t$  was 0. After confirming the end of a temperature rise of the molten aluminum due to a chemical reaction, the molten aluminum was left so as to be solidified in the crucible, and cooled into an ingot made of an aluminum alloy I.

(c) The ingot was taken out of the crucible, and extruded in a hot extrusion process at a temperature of  $500^{\circ}\text{C}$  with an extrusion ratio of 11, thereby producing an extruded round rod having a diameter of 9 mm.

(d) A specimen was produced from the extruded round rod, and its metallic structure was observed using a TEM. As a result, it was confirmed that no ultra-fine TiB-base particles 2 were present, but only countless fine TiB-base particles 3 were scattered, in an aluminum-base matrix 1. The fine TiB-base particles 3 had a maximum particle diameter of  $1.2\ \mu\text{m}$  and an average particle diameter of  $0.4\ \mu\text{m}$ .

The specimen was subjected to elemental analyses by EDX. The results of the elemental analyses indicate that the aluminum-base matrix 1 is composed of Al and Ti, and the fine TiB-base particles 3 are composed of Ti and B and do not contain Fe and Si.

(e) The extruded round rod was machined into a sample for use in a tensile test JIS 14A. The sample had a gage length  $L$  of 22 mm and a diameter  $D$  of 4.0 mm. The tensile test conducted on the sample indicated that the sample had a 0.2 %-offset yield strength  $\sigma_{0.2}$  of 307 MPa.

FIG. 8 shows a comparison between the 0.2 %-offset yield strengths  $\sigma_{0.2}$  of the aluminum alloy I according to Inventive Example 1 and the aluminum alloy I according to Comparative Example 1. It can be understood from FIG. 8 that the 0.2 %-offset yield strength  $\sigma_{0.2}$  of the aluminum alloy I according to Inventive Example 1 is about 2.1 times that of the aluminum alloy I according to Comparative Example 1.

#### [Inventive Example 2]

(a) Using a crucible, a molten aluminum alloy composed of 0.1 g of Fe, 0.05 g of Si, and 200 g of Al was prepared at  $900^{\circ}\text{C}$  in an Ar gas atmosphere.

(b) To the molten aluminum alloy, there were simultaneously added 96 g of Ti powder having a particle diameter of  $100\ \mu\text{m}$  or less and 43 g of B powder having a particle diameter of  $44\ \mu\text{m}$  or less. Then, the molten aluminum alloy was stirred using a stirring rod. The ratio  $(f + s)/t$  was 0.001. After confirming the end of a temperature rise of the molten aluminum alloy due

to a chemical reaction, the molten aluminum alloy was left so as to be solidified in the crucible, and cooled into an ingot made of an aluminum alloy II.

(c) The ingot was taken out of the crucible, and extruded in a hot extrusion process at a temperature of  $500^{\circ}\text{C}$  with an extrusion ratio of 11, thereby producing an extruded round rod having a diameter of 9 mm.

(d) A specimen was produced from the extruded round rod, and its metallic structure was observed using TEM. As a result, it was confirmed, as is the case with the specimen as shown in FIGS. 2 and 3, that countless ultra-fine TiB-base particles 2 and countless fine TiB-base particles 3 were dispersed in an aluminum-base matrix 1. The ultra-fine TiB-base particles 2 had a maximum particle diameter of 50 nm and an average particle diameter of 20 nm, and the fine TiB-base particles 3 had a maximum particle diameter of  $1.2\ \mu\text{m}$  and an average particle diameter of  $0.8\ \mu\text{m}$ .

The specimen was subjected to elemental analyses by EDX. The results of the elemental analyses indicate that the aluminum-base matrix 1 is composed of Al and Ti, the ultra-fine TiB-base particles 2 are composed of Ti and B and contains Fe and Si, and the fine TiB-base particles 3 are composed of Ti and B and do not contain Fe and Si.

(e) The extruded round rod was machined into a sample for use in a tensile test JIS 14A. The sample had a gage length  $L$  of 22 mm and a diameter  $D$  of 4.0 mm. The tensile test conducted on the sample indicated that the sample had a 0.2 %-offset yield strength  $\sigma_{0.2}$  of 453 MPa.

#### [Comparative Example 2]

An aluminum alloy II according to Comparative Example 2 was manufactured and its characteristics were inspected as follows:

(a) Using a crucible, 200 g of molten aluminum composed of pure aluminum having a purity of 99.99 % was prepared at  $900^{\circ}\text{C}$  in an Ar gas atmosphere.

(b) To the molten aluminum, there were simultaneously added 96 g of Ti powder having a particle diameter of  $100\ \mu\text{m}$  or less and 43 g of B powder having a particle diameter of  $44\ \mu\text{m}$  or less. Then, the molten aluminum was stirred using a stirring rod. The ratio  $(f + s)/t$  was 0. After confirming the end of a temperature rise of the molten aluminum due to a chemical reaction, the molten aluminum was left so as to be solidified in the crucible, and cooled into an ingot made of an aluminum alloy II.

(c) The ingot was taken out of the crucible, and extruded in a hot extrusion process at a temperature of 500 °C with an extrusion ratio of 11, thereby producing an extruded round rod having a diameter of 9 mm.

(d) A specimen was produced from the extruded round rod, and its metallic structure was observed using a TEM. As a result, it was confirmed that no ultra-fine TiB-base particles 2 were present, but only countless fine TiB-base particles 3 were dispersed, in an aluminum-base matrix 1. The fine TiB-base particles 3 had a maximum particle diameter of 1.2  $\mu\text{m}$  and an average particle diameter of 0.8  $\mu\text{m}$ .

The specimen was subjected to elemental analyses by EDX. The results of the elemental analyses indicate that the aluminum-base matrix 1 is composed of Al and Ti, and the fine TiB-base particles 3 are composed of Ti and B and do not contain Fe and Si.

(e) The extruded round rod was machined into a sample for use in a tensile test JIS 14A. The sample had a gage length L of 22 mm and a diameter D of 4.0 mm. The tensile test conducted on the sample indicated that the sample had a 0.2 %-offset yield strength  $\sigma_{0.2}$  of 180 MPa.

FIG. 9 shows a comparison between the 0.2 %-offset yield strengths  $\sigma_{0.2}$  of the aluminum alloy II according to Inventive Example 2 and the aluminum alloy II according to Comparative Example 2. A study of FIG. 9 indicates that the 0.2 %-offset yield strength  $\sigma_{0.2}$  of the aluminum alloy II according to Inventive Example 2 is about 2.5 times that of the aluminum alloy II according to Comparative Example 2. Based on this finding, the lower limit of the range of ratios  $(f + s)/t$  is set to 0.001.

#### [Inventive Example 3]

(a) Using a crucible, a molten aluminum alloy composed of 28 g of Fe, 2.8 g of Si, and 200 g of Al was prepared at 900 °C in an Ar gas atmosphere.

(b) To the molten aluminum alloy, there were simultaneously added 96 g of Ti powder having a particle diameter of 100  $\mu\text{m}$  or less and 43 g of B powder having a particle diameter of 44  $\mu\text{m}$  or less. Then, the molten aluminum alloy was stirred using a stirring rod. The ratio  $(f + s)/t$  was 0.3. After confirming the end of a temperature rise of the molten aluminum alloy due to a chemical reaction, the molten aluminum alloy was left so as to be solidified in the crucible, and cooled into an ingot made of an aluminum alloy III.

(c) The ingot was taken out of the crucible, and extruded in a hot extrusion process at a temperature of 500 °C with an extrusion ratio of 11, thereby producing an extruded round rod having a diameter of 9 mm.

(d) A specimen was produced from the extruded round rod, and its metallic structure was observed using TEM. As a result, it was confirmed, as is the case with the specimen as shown in FIGS. 2 and 3, that countless ultra-fine TiB-base particles 2 and countless fine TiB-base particles 3 were dispersed in an aluminum-base matrix 1. The ultra-fine TiB-base particles 2 had a maximum particle diameter of 50 nm and an average particle diameter of 20 nm, and the fine TiB-base particles 3 had a maximum particle diameter of 1.2  $\mu\text{m}$  and an average particle diameter of 0.8  $\mu\text{m}$ .

The specimen was subjected to elemental analyses by EDX. The results of the elemental analyses indicate that the aluminum-base matrix 1 is composed of Al and Ti, the ultra-fine TiB-base particles 2 are composed of Ti and B and contain Fe and Si, and the fine TiB-base particles 3 are composed of Ti and B and do not contain Fe and Si.

(e) The extruded round rod was machined into a sample for use in a tensile test JIS 14A. The sample had a gage length L of 22 mm and a diameter D of 4.0 mm. The tensile test conducted on the sample indicated that the sample had a 0.2 %-offset yield strength  $\sigma_{0.2}$  of 500 MPa.

#### [Comparative Example 3]

An aluminum alloy III according to Comparative Example 3 was manufactured and its characteristics were inspected as follows:

(a) Using a crucible, a molten aluminum alloy composed of 44.7 g of Fe, 5.6 g of Si, and 200 g of Al was prepared at 900 °C in an Ar gas atmosphere.

(b) To the molten aluminum, there were simultaneously added 96 g of Ti powder having a particle diameter of 100  $\mu\text{m}$  or less and 43 g of B powder having a particle diameter of 44  $\mu\text{m}$  or less. Then, the molten aluminum was stirred using a stirring rod. The ratio  $(f + s)/t$  was 0.5. After confirming the end of a temperature rise of the molten aluminum due to a chemical reaction, the molten aluminum was left so as to be solidified in the crucible, and cooled into an ingot made of an aluminum alloy III.

(c) The ingot was taken out of the crucible, and extruded in a hot extrusion process at a temperature of 500 °C with an extrusion ratio of 11, thereby producing an extruded round rod having

a diameter of 9 mm.

(d) A specimen was produced from the extruded round rod, and its metallic structure was observed using a TEM. As a result, it was confirmed that countless ultra-fine TiB-base particles 2, countless fine TiB-base particles 3, and countless coarse intermetallic compound bodies were dispersed in an aluminum-base matrix 1. The ultra-fine TiB-base particles 2 had a maximum particle diameter of 50 nm and an average particle diameter of 20 nm. The fine TiB-base particles 3 had a maximum particle diameter of 1.2  $\mu\text{m}$  and an average particle diameter of 0.8  $\mu\text{m}$ . The coarse intermetallic compound bodies had longest portions whose length was 500  $\mu\text{m}$ .

The specimen was subjected to elemental analyses by EDX. The results of the elemental analyses indicate that the aluminum-base matrix 1 is composed of Al and Ti, the ultrafine TiB-base particles 2 are composed of Ti and B and contain Fe and Si, the fine TiB-base particles 3 are composed of Ti and B and do not contain Fe and Si, and the coarse intermetallic compound bodies are composed of Al and Fe.

(e) The extruded round rod was machined into a sample for use in a tensile test JIS 14A. The sample had a gage length L of 22 mm and a diameter D of 4.0 mm. The tensile test conducted on the sample indicated that the sample had a 0.2 %-offset yield strength  $\sigma_{0.2}$  of 318 MPa.

FIG. 10 shows a comparison between the 0.2 %-offset yield strengths  $\sigma_{0.2}$  of the aluminum alloy III according to Inventive Example 3 and the aluminum alloy III according to Comparative Example 3. A study of FIG. 10 indicates that the 0.2 %-offset yield strength  $\sigma_{0.2}$  of the aluminum alloy III according to Inventive Example 3 is about 1.5 times that of the aluminum alloy III according to Comparative Example 3. Based on this finding, the upper limit of the range of ratios  $(f + s)/t$  is set to 0.3.

#### [Inventive Example 4]

(a) Using a crucible, a molten aluminum alloy composed of 0.15 g of Fe and 380 g of Al was prepared at 700 °C in an Ar gas atmosphere.

(b) To the molten aluminum alloy, there were simultaneously added 480 g of  $\text{K}_2\text{TiF}_6$  powder having a particle diameter of 500  $\mu\text{m}$  or less and 504 g of  $\text{KBF}_4$  powder having a particle diameter of 500  $\mu\text{m}$  or less. Then, the molten aluminum alloy was stirred using a stirring rod. The ratio  $(f + s)/t$  was 0.001. After confirming the end of a temperature rise of the molten aluminum alloy due to a chemical reaction, the molten aluminum alloy was left so as to be

solidified in the crucible, and cooled into an ingot made of an aluminum alloy IV.

(c) The ingot was taken out of the crucible, and extruded in a hot extrusion process at a temperature of 500 °C with an extrusion ratio of 11, thereby producing an extruded round rod having a diameter of 9 mm.

(d) A specimen was produced from the extruded round rod, and its metallic structure was observed using a TEM. As a result, it was confirmed, as is the case with the specimen as shown in FIGS. 2 and 3, that countless ultra-fine TiB-base particles 2 and countless fine TiB-base particles 3 were dispersed in an aluminum-base matrix 1. The ultra-fine TiB-base particles 2 had a maximum particle diameter of 50 nm and an average particle diameter of 20 nm, and the fine TiB-base particles 3 had a maximum particle diameter of 1.2  $\mu\text{m}$  and an average particle diameter of 0.4  $\mu\text{m}$ .

The specimen was subjected to elemental analyses by EDX. The results of the elemental analyses indicate that the aluminum-base matrix 1 is composed of Al and Ti, the ultra-fine TiB-base particles 2 are composed of Ti and B and contain Fe, and the fine TiB-base particles 3 are composed of Ti and B and do not contain Fe.

(e) The extruded round rod was machined into a sample for use in a tensile test JIS 14A. The sample had a gage length L of 22 mm and a diameter D of 4.0 mm. The tensile test conducted on the sample indicated that the sample had a 0.2 %-offset yield strength  $\sigma_{0.2}$  of 638 MPa.

Although certain preferred embodiments of the present invention has been shown and described in detail, it should be understood that various changes and modifications may be made therein without departing from the scope of the appended claims.

#### Claims

1. A high-strength aluminum alloy comprising:  
an aluminum-base matrix; and  
TiB-base particles dispersed in said aluminum-base alloy and containing either Fe or Fe and Si.
2. A high-strength aluminum alloy according to claim 1, wherein a ratio  $(f + s)/t$  is in the range of  $0.001 \leq (f + s)/t \leq 0.3$  where f represents the amount of Fe expressed by a gram atomic weight, s represents the amount of Si expressed by a gram atomic weight (including s = 0), and t represents the amount of Ti expressed by a gram atomic weight.

3. A high-strength aluminum alloy according to claim 1 or 2, wherein said TiB-base particles have a particle diameter  $d$  in the range of  $d \leq 50$  nm.
4. A high-strength aluminum alloy according to claim 1, wherein said aluminum-base matrix is made of Al and Ti.
5. A high-strength aluminum alloy comprising:
  - an aluminum-base matrix;
  - ultra-fine TiB-base particles dispersed in said aluminum-base matrix and having a maximum particle diameter of 50 nm; and
  - fine TiB-base particles dispersed in said aluminum-base matrix and having a maximum particle diameter of  $1.2 \mu\text{m}$ .
6. A high-strength aluminum alloy according to claim 5, wherein said aluminum-base matrix is composed of Al and Ti.
7. A high-strength aluminum alloy according to claim 5, wherein said ultra-fine TiB-base particles are composed of Ti and B and contain Fe.
8. A high-strength aluminum alloy according to claim 5, wherein said ultra-fine TiB-base particles are composed of Ti and B and contain Fe and Si.
9. A high-strength aluminum alloy according to claim 5, wherein said fine TiB-base particles are composed of Ti and B and free of Fe.
10. A high-strength aluminum alloy according to claim 5, wherein said fine TiB-base particles are composed of Ti and B and free of Fe and Si.
11. A method of manufacturing a high-strength aluminum alloy, comprising the steps of:
  - preparing a molten aluminum alloy containing Fe; and
  - adding at least one of Ti and a Ti-containing compound and at least one of B and B-containing compound to said molten aluminum alloy, thus producing TiB-base particles containing Fe.
12. A method according to claim 11, wherein a ratio  $f/t$  is in the range of  $0.001 \leq f/t \leq 0.3$  where  $f$  represents the amount of Fe expressed by a gram atomic weight, and  $t$  represents the amount of Ti expressed by a gram atomic weight.
13. A method of manufacturing a high-strength aluminum alloy, comprising the steps of:
  - preparing a molten aluminum alloy containing Fe and Si; and
  - adding at least one of Ti and a Ti-containing compound and at least one of B and B-containing compound to said molten aluminum alloy, thus producing either both TiB-base particles containing Fe and TiB-base particles containing Fe and Si, or TiB-base particles containing Fe and Si.
14. A method according to claim 13, wherein a ratio  $(f + s)/t$  is in the range of  $0.001 \leq (f + s)/t \leq 0.3$  where  $f$  represents the amount of Fe expressed by a gram atomic weight,  $s$  represents the amount of Si expressed by a gram atomic weight (including  $s = 0$ ), and  $t$  represents the amount of Ti expressed by a gram atomic weight.
15. A method according to claim 11, 12, 13, or 14, wherein said Ti-containing compound comprises  $\text{K}_2\text{TiF}_6$  and said B-containing compound comprises  $\text{KBF}_4$ .



FIG. 1

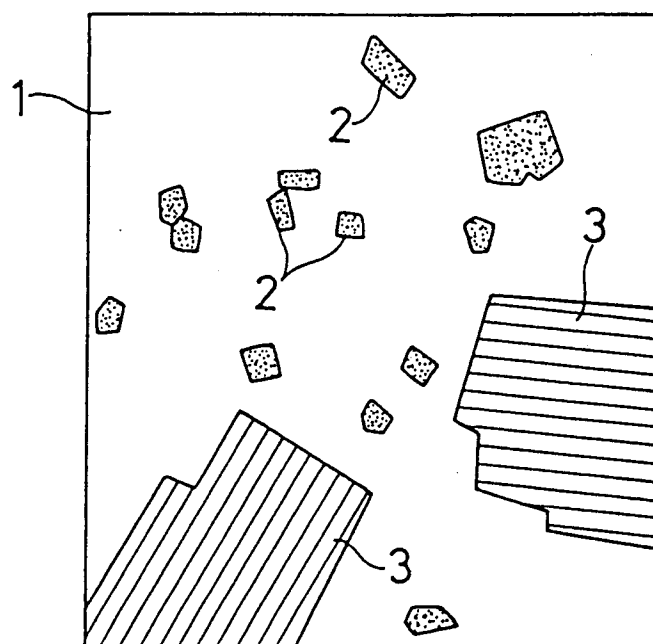


FIG. 2



FIG. 3

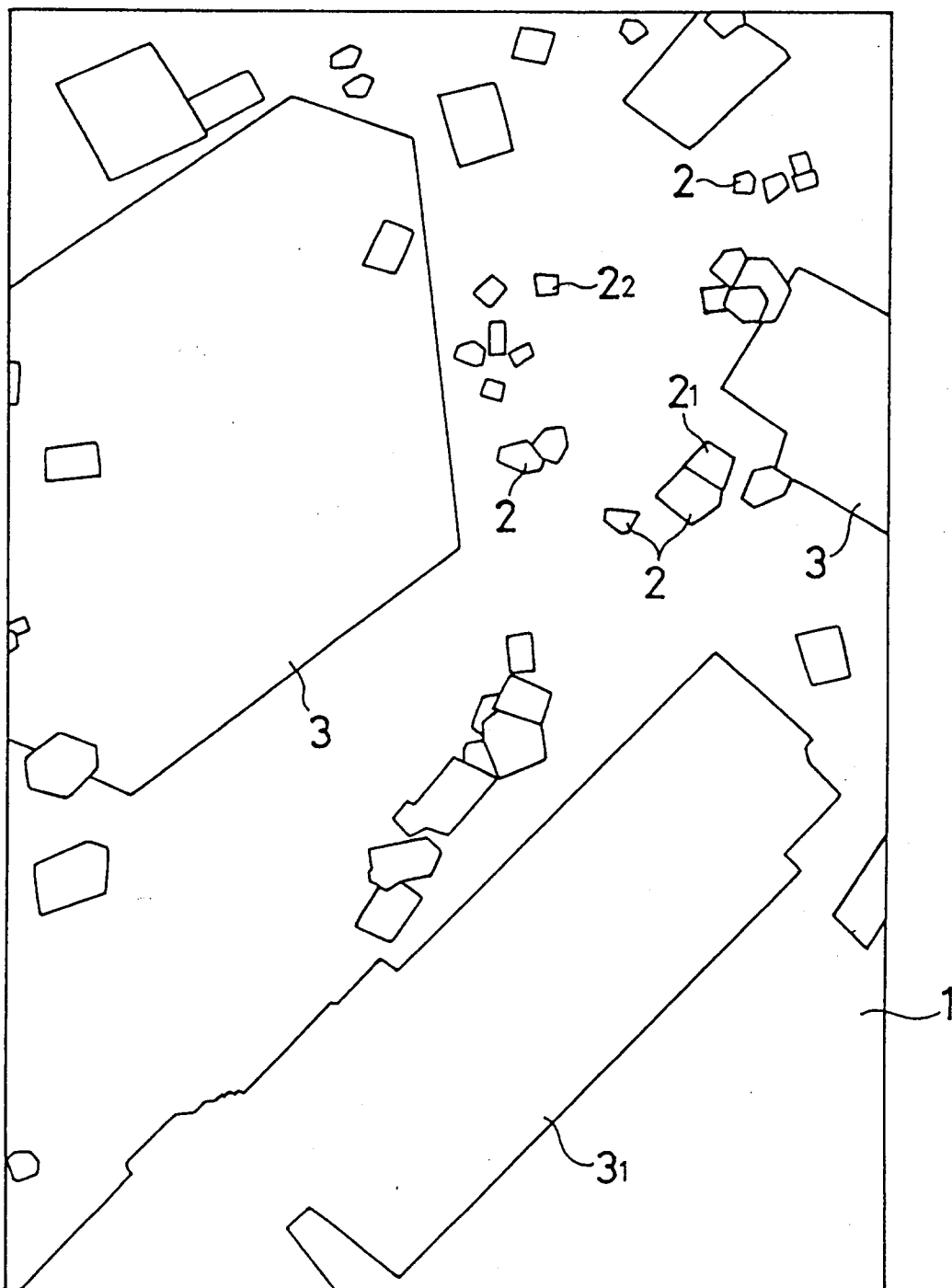


FIG. 4

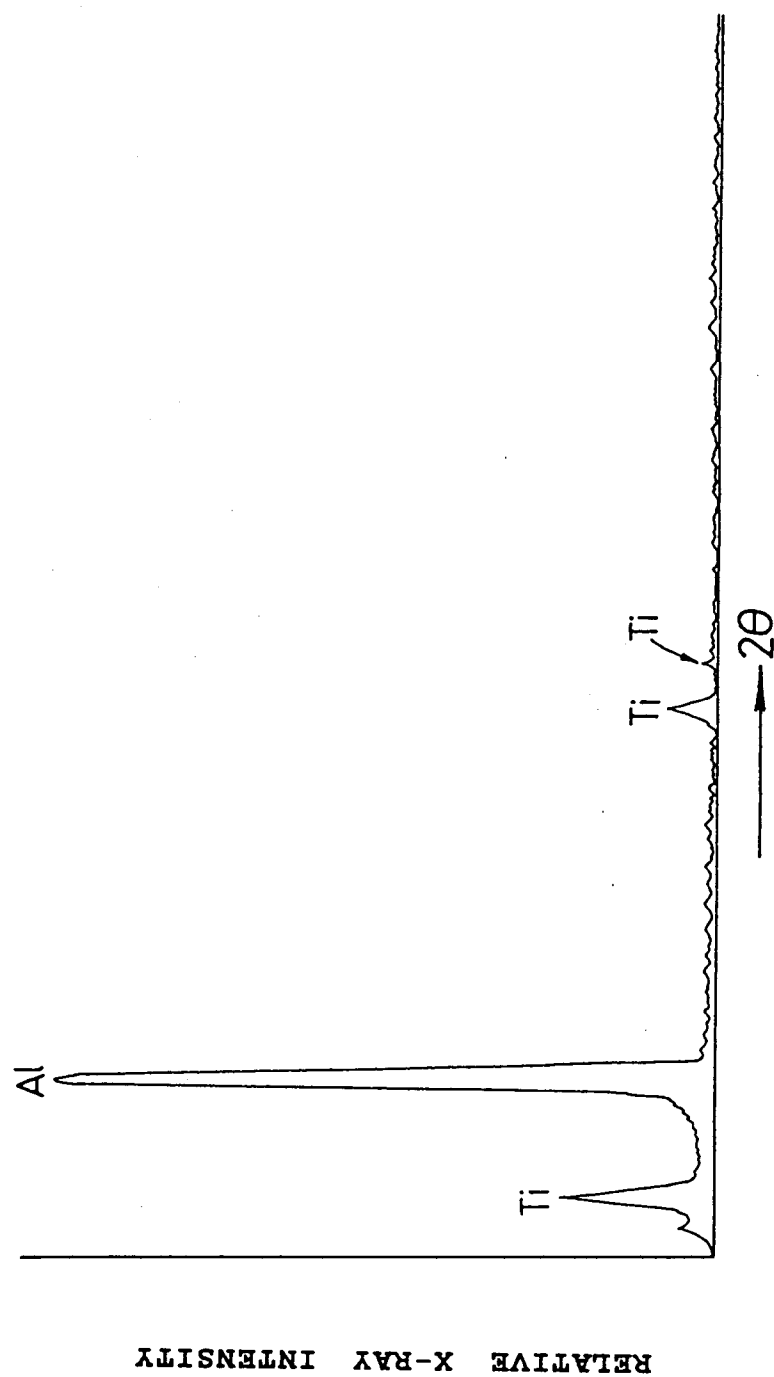


FIG. 5

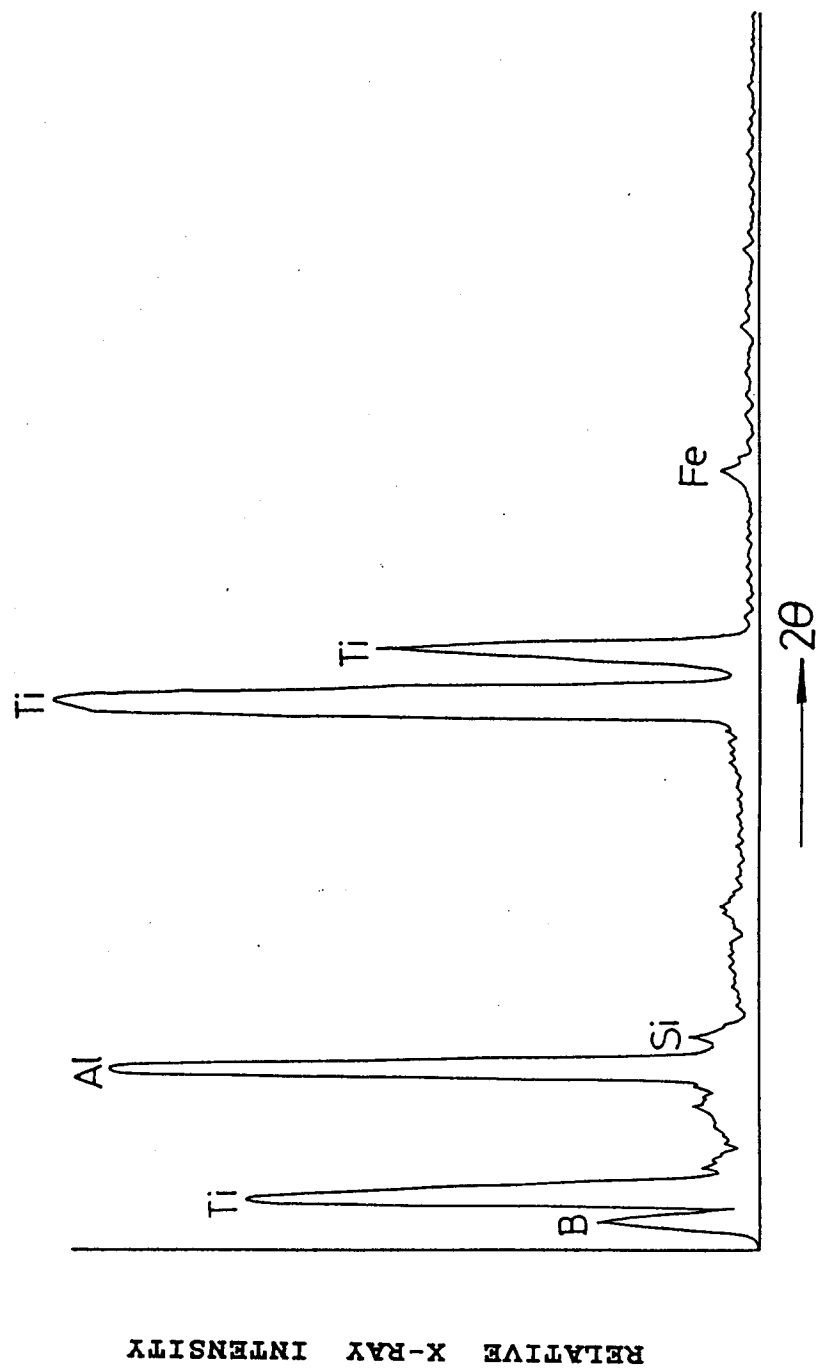


FIG. 6

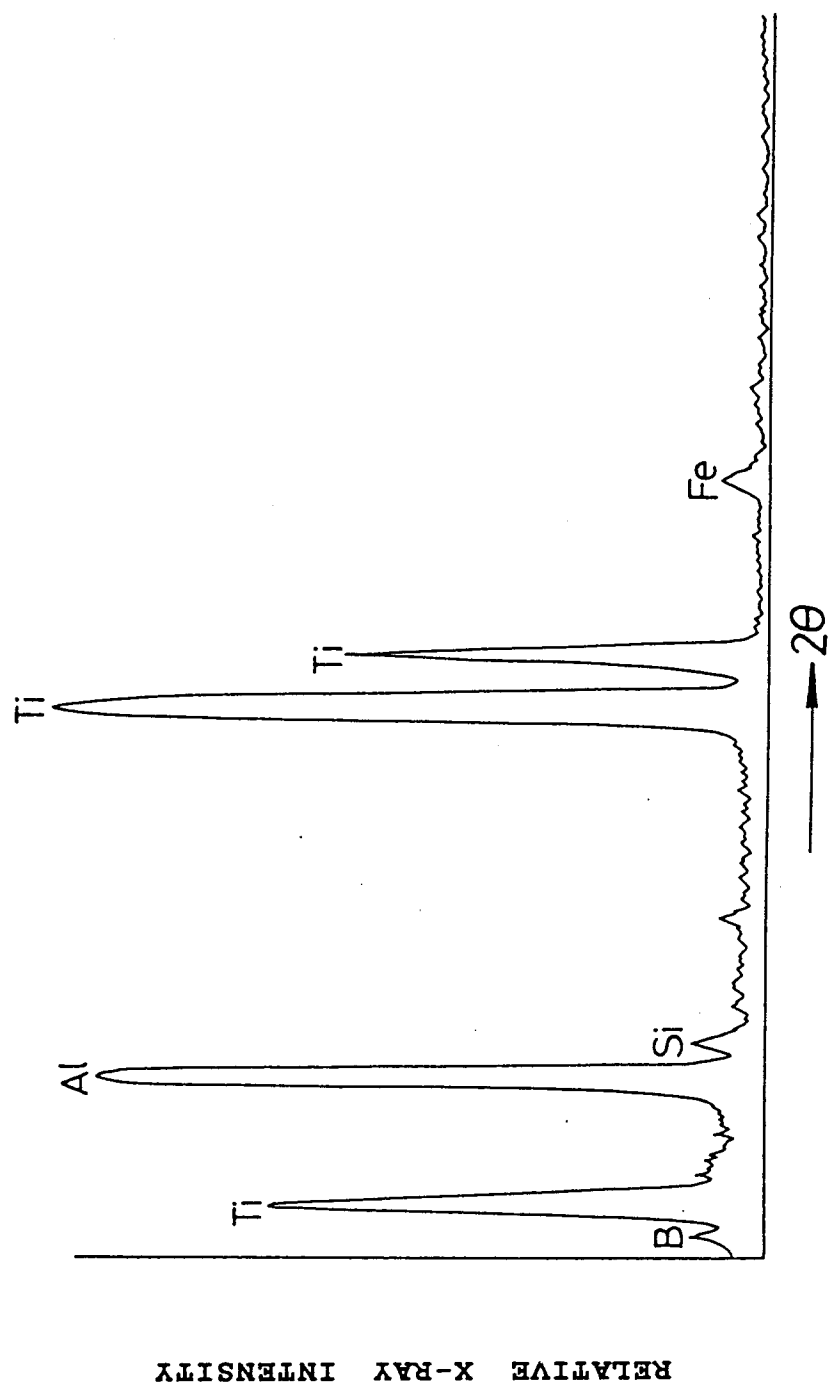


FIG. 7

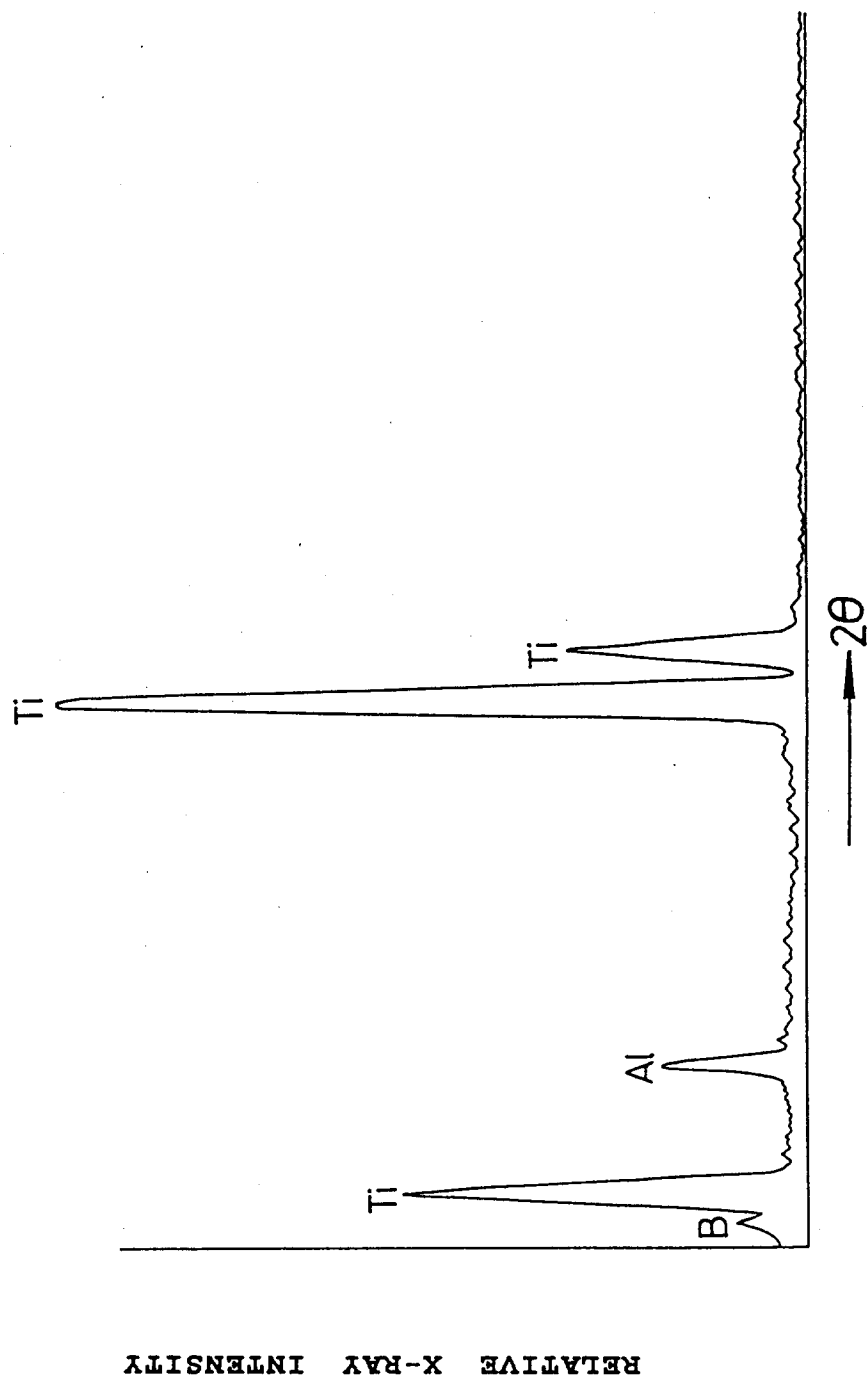


FIG. 8

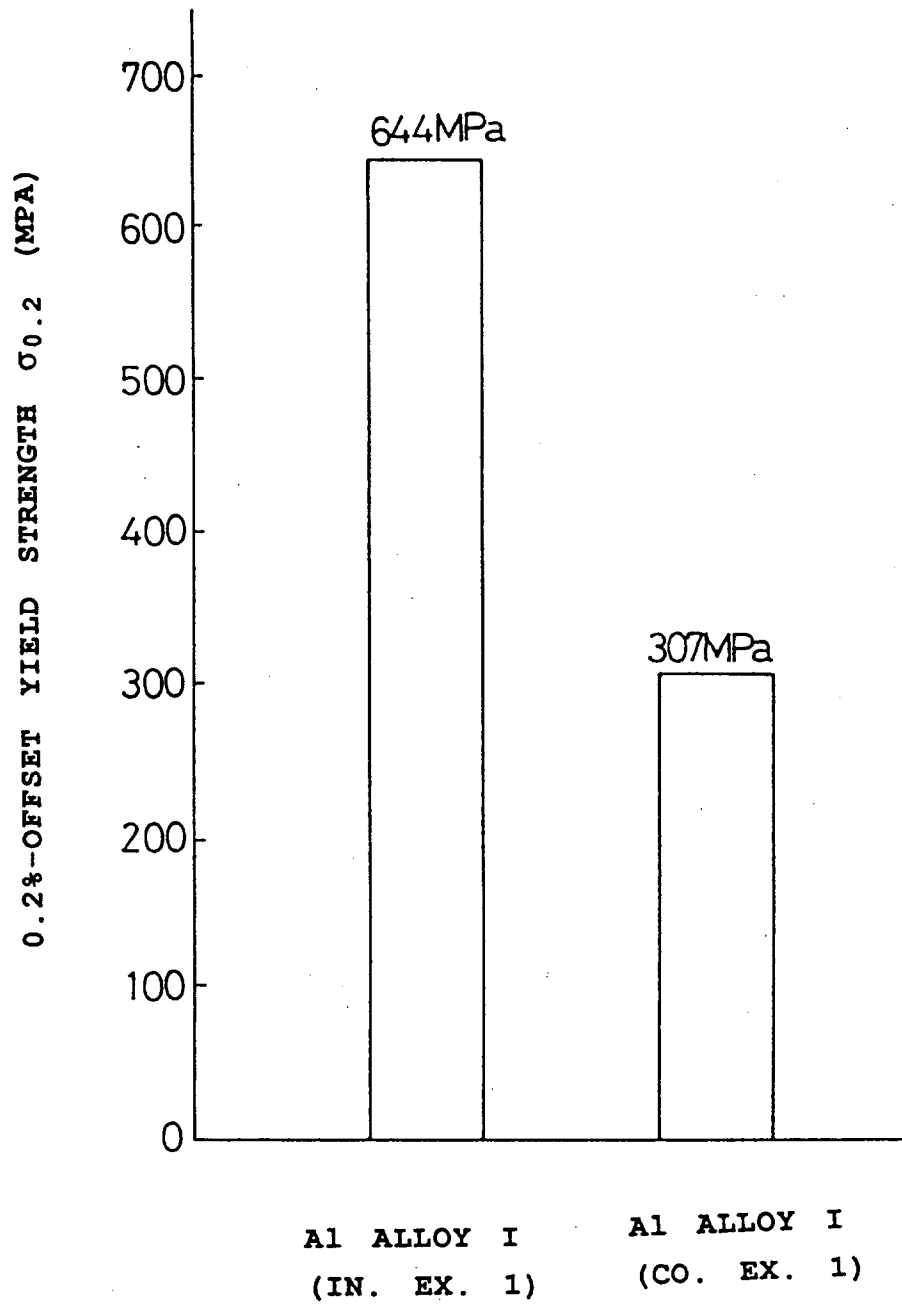




FIG. 9

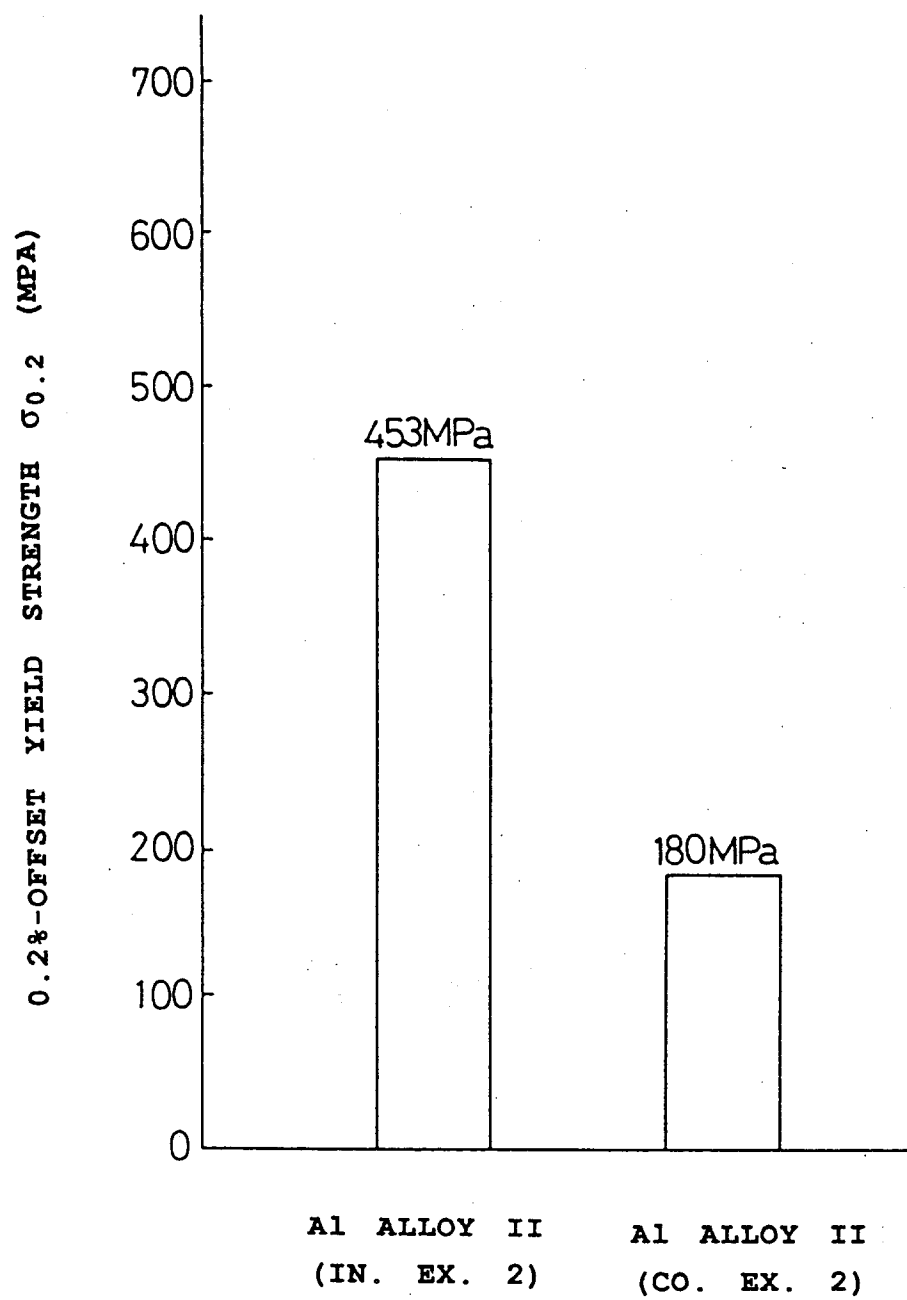
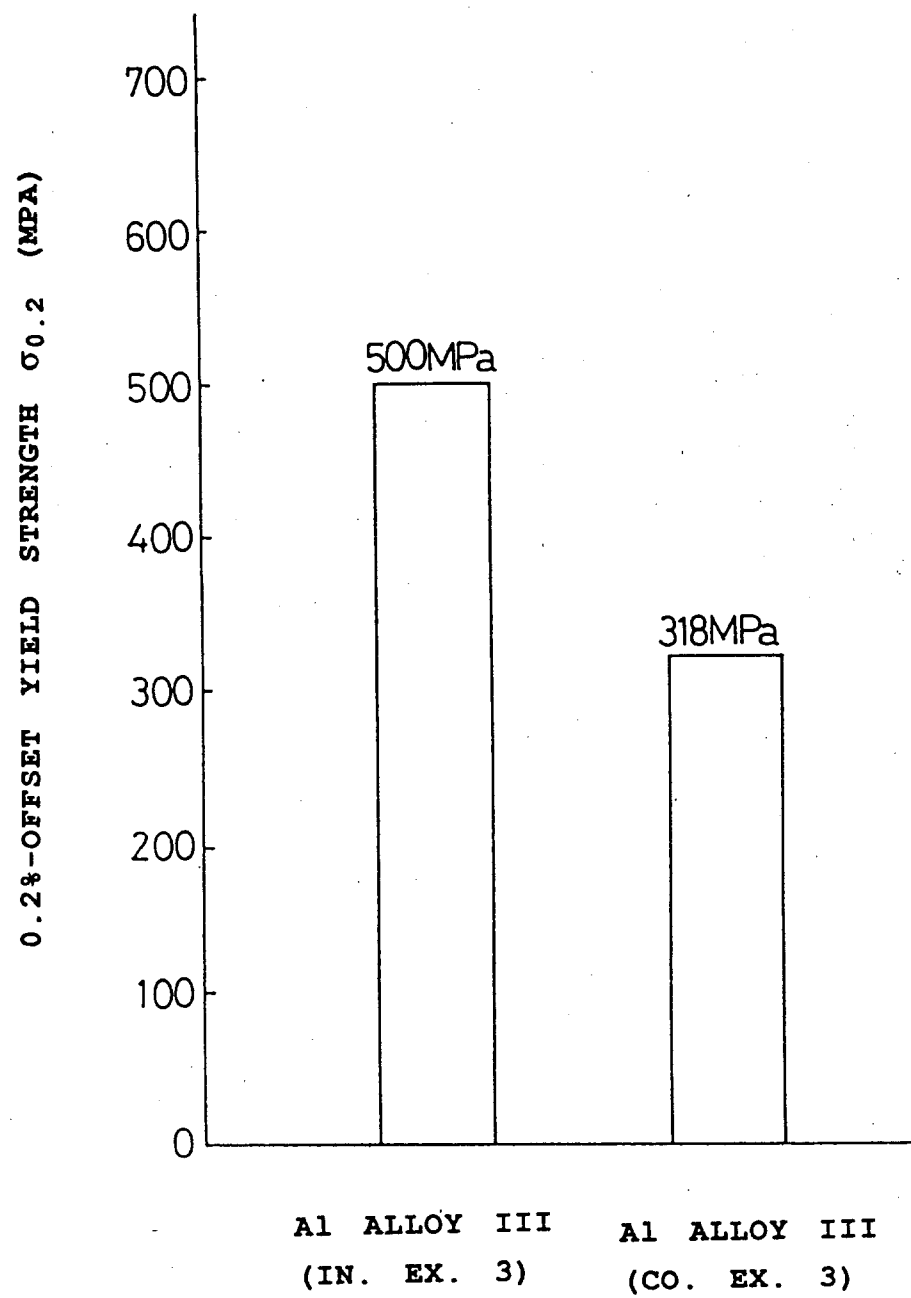


FIG. 10





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# EUROPEAN SEARCH REPORT

Application Number  
EP 95 10 3195

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	<p>GIESSEREI FOSCHUNG, GIESSEREI-VERLAG G.M.B.H., DÜSSELDORF, vol. 32, no. 2, 1980 DE, pages 53-60, REIF, W., SCHNEIDER, W. 'Investigations foe interpretation of the process of grain refinement of aluminium by AlTiB master alloys' *Pages 53, 54, 59 and 60*</p> <p>---</p>	1-15	C22C21/00 C22C1/03
X	<p>PATENT ABSTRACTS OF JAPAN vol. 6 no. 127 (C-113) ,13 July 1982 &amp; JP-A-57 054235 (MITSUBISHI K.K.) 31 March 1982, *Table 2 of patent document* * abstract *</p> <p>---</p>	1-15	
A	<p>US-A-5 055 256 (SIGWORTH,G., GUZOWSKI,M.) 8 October 1991 *Col.3, lines 7-27*</p> <p>---</p>	1-15	
A	<p>INTERNATIONAL JOURNAL OF RAPID SOLIDIFICATION , vol. 7, no. 4, 1993 GB, pages 245-254, CANTOR, B., KIM, W.T., BRIFFITH, W.D., JOLLY, M.R. 'TEM characterization of melt spun Al-3Ti-1B and Al-5Ti-1B alloys'</p> <p>---</p>	1-15	<p>TECHNICAL FIELDS SEARCHED (Int.Cl.6)</p> <p>C22C</p>
A	<p>PATENT ABSTRACTS OF JAPAN vol. 12 no. 398 (C-538) ,21 October 1988 &amp; JP-A-63 140059 (NIPPON LIGHT METAL CO. LTD.) 11 June 1988, *Note Tables in patent document* * abstract *</p> <p>---</p> <p style="text-align: center;">-/--</p>	1-15	
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 17 July 1995	Examiner Badcock, G
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p>		<p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>.....</p> <p>&amp; : member of the same patent family, corresponding document</p>	



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## EUROPEAN SEARCH REPORT

Application Number  
EP 95 10 3195

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	PATENT ABSTRACTS OF JAPAN vol. 11 no. 361 (C-459) ,25 November 1987 & JP-A-62 133037 (NGK INSULATORS LTD.) 16 June 1987, * abstract *	1-15	
A	--- PATENT ABSTRACTS OF JAPAN vol. 3 no. 7 (C-034) ,24 January 1979 & JP-A-53 132419 (SUMITOMO ELECTRIC IND. LTD.) 18 November 1978, * abstract * -----	1-15	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
Place of search MUNICH		Date of completion of the search 17 July 1995	Examiner Badcock, G
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document			