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# **EUROPEAN PATENT APPLICATION**

published in accordance with Art. 153(4) EPC

(43) Date of publication: 22.05.2019 Bulletin 2019/21

(21) Application number: 17827456.9

(22) Date of filing: 30.06.2017

(51) Int Cl.: C22C 21/00<sup>(2006.01)</sup> C22F 1/00<sup>(2006.01)</sup>

C22F 1/04 (2006.01)

(86) International application number: PCT/JP2017/024184

(87) International publication number: WO 2018/012326 (18.01.2018 Gazette 2018/03)

(84) Designated Contracting States:

AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

Designated Extension States:

**BAME** 

**Designated Validation States:** 

MA MD

(30) Priority: 12.07.2016 JP 2016137522

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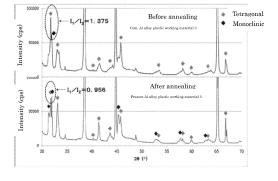
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## (54) ALUMINUM ALLOY PLASTIC WORKING MATERIAL AND PRODUCTION METHOD THEREFOR

(57) The present invention provides an aluminum alloy plastic working material which has a low Young's modulus, but has superior proof stress, and a method for efficiently producing the aluminum alloy plastic working material. The aluminum alloy plastic working material according to the present invention contains 5.0-10.0 wt% of Ca, the balance being aluminum and incidental impurities, and has 25% or more by volume of an  $AI_4Ca$  phase

which is a dispersed phase. The  $Al_4Ca$  phase comprises a tetragonal  $Al_4Ca$  phase and a monoclinic  $Al_4Ca$  phase, and the intensity ratio (11/12) of the highest diffraction peak (11) attributed to the tetragonal system to the highest diffraction peak (12) attributed to the monoclinic system, which are obtained by an X-ray diffraction measurement, is one or less.

[FIG. 2]



## Description

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#### FIELD OF THE INVENTION

<sup>5</sup> **[0001]** The present invention relates to an aluminum alloy plastic working material which has a low Young's modulus, but has an excellent proof stress, and relates to a method for producing the working material.

**[0002]** Since aluminum has many excellent characteristics such as corrosion resistance, electric conductivity, thermal conductivity, light weight, brightness and machinability, aluminum is used for various purposes. In addition, since plastic deformation resistance is small, various shapes can be imparted, and aluminum is also widely used for members subjected to plastic working such as bending processing.

**[0003]** Here, when the rigidity of the aluminum alloy is high, there is a problem that the spring back amount increases when the plastic working such as bending processing is performed, and thus it is difficult to obtain dimensional accuracy. Under such circumstances, an aluminum alloy material having a low Young's modulus is desired, and a method for lowering the Young's modulus of the aluminum alloy material has been studied.

[0004] For example, Patent Literature 1 (JP 2011-105982 A) proposes an aluminum alloy containing an A1 phase and an Al<sub>4</sub>Ca phase, wherein the Al<sub>4</sub>Ca phase contains an Al<sub>4</sub>Ca crystallized product, and an average value of the longer side of the Al<sub>4</sub>Ca crystallized product is 50 μm or less.

**[0005]** In the aluminum alloy disclosed in the above Patent Literature 1, the movement of the Al<sub>4</sub>Ca crystallized product accompanying the dislocation in the matrix becomes easy, so that the rolling workability of the aluminum alloy can be remarkably improved.

CITATION LIST

Patent Literature

[0006] Patent Literature 1: JP 2011-105982 A

SUMMARY OF INVENTION

30 Technical Problem

**[0007]** However, as represented by, for example, terminals of electrical equipment, the requirement for the dimensional accuracy of the product where aluminum alloys are used has been strict year by year, so that aluminum alloys with lower rigidity are required while maintaining proof stress. Under such technical background, the current situation is that the aluminum alloy of Patent Literature 1 cannot sufficiently satisfy the above requirements.

**[0008]** Considering the above problems in the prior arts, an object of the present invention is to provide an aluminum alloy plastic working material which has a low Young's modulus, but has an excellent proof stress, and relates to a method for efficiently producing the working material.

40 Solution to Problem

**[0009]** As a result of extensive study with respect to the aluminum alloy plastic working material and production method therefor in order to achieve the above object, the present inventors have found that it is extremely effective that an Al<sub>4</sub>Ca phase is used as the dispersed phase and the crystal structure of the Al<sub>4</sub>Ca phase is appropriately controlled, and have reached the present invention.

[0010] Namely, the present invention is to provide an aluminum alloy plastic working material, which comprises:

5.0 to 10.0 wt% of Ca, and

the remainder aluminum and unavoidable impurities,

a volume ratio of an  ${\rm Al_4Ca}$  phase, which is a dispersed phase, is 25% or more,

the Al<sub>4</sub>Ca phase comprises a tetragonal Al<sub>4</sub>Ca phase and a monoclinic Al<sub>4</sub>Ca phase, and

an intensity ratio  $(I_1/I_2)$  of the highest diffraction peak  $(I_1)$  attributed to the tetragonal system to the highest diffraction peak  $(I_2)$  attributed to the monoclinic system, which are obtained by an X-ray diffraction measurement, is 1 or less.

[0011] By addition of Ca, a compound of Al<sub>4</sub>Ca is prepared, which has an activity to lower the Young's modulus of the aluminum alloy. The effect becomes remarkable when the content of Ca is 5.0% or more. To the contrary, when added in excess of 10.0%, the casting property decreases, and since particularly casting by continuous casting such as DC casting becomes difficult, it is necessary to produce by a method with a high production cost such as powder metallurgy

method. In the case of producing by the powder metallurgy method, there is a risk that oxides formed on the surface of the alloy powder may get mixed in the product, which may lower the proof stress.

**[0012]** In the aluminum alloy plastic working product of the present invention, though the crystal structure of the  $Al_4Ca$  phase which is used as the dispersed phase is basically a tetragonal crystal, the present inventors have intensively studied and found that when the crystal structure of the  $Al_4Ca$  phase contains a monoclinic crystal, the proof stress do not decrease so much, but the Young's modulus is greatly decreased. Here, when the intensity ratio  $(l_1/l_2)$  of the highest diffraction peak  $(l_1)$  attributed to the tetragonal system to the highest diffraction peak  $(l_2)$  attributed to the monoclinic system, which are obtained by an X-ray diffraction measurement, is 1 or less, the Young's modulus can be greatly lowered while maintaining the proof stress.

[0013] Further, it is preferable that the aluminum alloy plastically working material of the present invention further contains at least one or more of Fe: 0.05 to 1.0 wt% and Ti: 0.005 to 0.05 wt%.

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**[0014]** When Fe is contained in the aluminum alloy, the casting property can be improved by broadening the solidification temperature range (solid-liquid coexisting region), and thus the casting surface of the ingot can also be improved. Further there is an effect that the dispersed crystallized product of Fe makes the eutectic structure uniform. The effect becomes remarkable when the Fe content is 0.05 wt% or more. To the contrary, when contained in excess of 1.0 wt%, the eutectic structure becomes coarse and there is a risk to lower the proof stress.

**[0015]** Ti acts as a refining material of the casted structure and exhibits an action to improve casting property, extrudability, and rolling property. The effect is remarkable when the Ti content is 0.005 wt% or more. To the contrary, even when added in excess of 0.05 wt%, it cannot be expected to increase the effect of refining the casted structure, and on the contrary, there is a risk that a coarse intermetallic compound which is to be the starting point of fracture may be generated. It is preferable that Ti is added by a rod hardener (Al-Ti-B alloy) during the casting. B added at this time together with Ti as the rod hardener is acceptable.

[0016] Further, in the aluminum alloy plastic working product of the present invention, it is preferable that an average crystal grain size of the  $Al_4Ca$  phase is 1.5  $\mu$ m or less. When the average grain size of the  $Al_4Ca$  phase becomes too large, the proof stress of the aluminum alloy decreases, but when the average grain size is 1.5  $\mu$ m or less, it is possible to suppress the decrease of the proof stress.

[0017] Further, the present invention provides a method for producing an aluminum alloy plastic working material, comprising:

a first step for obtaining a plastic workpiece of an aluminum alloy by subjecting an aluminum alloy ingot which contains 5.0 to 10.0 wt% of Ca with the remainder aluminum and inevitable impurities, and has a volume ratio of an  $Al_4Ca$  phase which is a dispersed phase of 25% or more to a plastic processing, and a second step for subjecting to a heat treatment in a temperature range of 100 to 300 °C.

[0018] After the first step for obtaining a plastic workpiece of an aluminum alloy by subjecting an aluminum alloy ingot which contains 5.0 to 10.0 wt% of Ca with the remainder aluminum and inevitable impurities, and has a volume ratio of an Al<sub>4</sub>Ca phase which is a dispersed phase of 25% or more to a plastic processing, by conducting the step for subjecting to a heat treatment in a temperature range of 100 to 300 °C (Second step), a part of the tetragonal Al<sub>4</sub>Ca phase can be changed into monoclinic crystal.

**[0019]** When the holding temperature in the second step is less than 100 °C, a change from a tetragonal to a monoclinic crystal is difficult to occur, and when the holding temperature is 300 °C or more, recrystallization of the aluminum base material occurs and there is a risk that the proof stress will be lowered. The more preferable temperature range of the heat treatment is 160 to 240 °C. Though the appropriate time for the heat treatment varies depending on the size and shape of the aluminum alloy material, it is preferable that the temperature of the aluminum alloy material itself is kept at least at the holding temperature for 1 hour or more.

**[0020]** In the method for producing the aluminum alloy plastic working material of the present invention, it is preferable that the aluminum alloy ingot contains at least one or more of Fe: 0.05 to 1.0 wt% and Ti: 0.005 to 0.05 wt%.

**[0021]** When Fe is contained in the aluminum alloy, the casting property can be improved by broadening the solidification temperature range (solid-liquid coexisting region), and thus the casting surface of the ingot can also be improved. Further there is an effect that the dispersed crystallized product of Fe makes the eutectic structure uniform. The effect becomes remarkable when the Fe content is 0.05 wt% or more. To the contrary, when contained in excess of 1.0 wt%, the eutectic structure becomes coarse and there is a risk to lower the proof stress.

**[0022]** Ti acts as a refining material of the casted structure and exhibits an action to improve casting property, extrudability, and rolling property. The effect is remarkable when the Ti content is 0.005 wt% or more. To the contrary, even when added in excess of 0.05 wt%, it cannot be expected to increase the effect of refining the casted structure, and on the contrary, there is a risk that a coarse intermetallic compound which is to be the starting point of fracture may be generated. It is preferable that Ti is added by a rod hardener (Al-Ti-B alloy) during the casting. B added at this time together with Ti as the rod hardener is acceptable.

**[0023]** Furthermore, in the method for producing an aluminum alloy plastic working material according to the present invention, it is preferable that, before the first step, the aluminum alloy ingot is not subjected to a heat treatment where the ingot is maintained at a temperature of 400 °C or more.

**[0024]** Generally, in the case of preparing an aluminum alloy, before the ingot is subjected to plastic working, a homogenization treatment is carried out where the ingot is held at a temperature of 400 to 600 °C, but when this homogenization treatment is performed, the  $Al_4Ca$  phase contained in the aluminum alloy tends to be large, and the average grain size becomes larger than 1.5  $\mu$ m. Since the proof stress reduces due to the increase in the average grain size, it is preferable that the homogenization treatment at a holding temperature of 400 °C or higher would not be performed.

Effects of the invention

**[0025]** According to the present invention, it is possible to provide an aluminum alloy plastic working material which has both an excellent proof stress and a low Young's modulus, and a method for efficiently producing the working material.

BRIEF DESCRIPTION OF THE DRAWINGS

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FIG. 1 is a process chart relating to the method of producing the aluminum alloy plastic working material of the present invention.

FIG. 2 is an X-ray diffraction pattern of the aluminum alloy plastic working material.

FIG. 3 is a photograph of the structure of the present aluminum alloy plastic working material 3.

FIG. 4 is a photograph of the structure of the comparative aluminum alloy plastic working material 3.

Embodiments for achieving the invention

**[0027]** Hereinafter, the aluminum alloy plastic working material and the method for producing therefor of the present invention will be described in detail with reference to the drawings, but the present inventions are not limited to only those.

1. Aluminum alloy plastically working material

(1) Composition

[0028] The aluminum alloy plastic working material includes 5.0 to 10.0 wt% of Ca, and the remainder aluminum and unavoidable impurities. In addition, it is preferable to further contain at least one or more of Fe: 0.05 to 1.0 wt% and Ti: 0.005 to 0.05 wt%.

[0029] Each component element will be explained below.

40 Ca: 5.0 to 10.0 wt% (preferably 6.0 to 8.0 wt%)

**[0030]** Ca forms a compound of  $Al_4$ Ca and has the activity to lower the Young's modulus of the aluminum alloy. The effect becomes remarkable when the content of Ca is 5.0% or more. To the contrary, when added in excess of 10.0%, the casting property decreases, and since particularly casting by continuous casting such as DC casting becomes difficult, it is necessary to produce by a method with a high production cost such as powder metallurgy method. In the case of producing by the powder metallurgy method, there is a risk that oxides formed on the surface of the alloy powder may get mixed in the product, which may lower the proof stress.

Fe: 0.05 to 1.0 wt%

**[0031]** When Fe is contained, the casting property can be improved by broadening the solidification temperature range (solid-liquid coexisting region), and thus the casting surface of the ingot can also be improved. Further there is an effect that the dispersed crystallized product of Fe makes the eutectic structure uniform. The effect becomes remarkable when being 0.05 wt% or more, and to the contrary, when contained in excess of 1.0 wt%, the eutectic structure becomes coarse and there is a risk to lower the proof stress.

Ti: 0.005 to 0.05 wt%

**[0032]** Ti acts as a refining material of the casted structure and exhibits an action to improve casting property, extrudability, and rolling property. The effect is remarkable when being 0.005 wt% or more, and to the contrary, even when added in excess of 0.05 wt%, it cannot be expected to increase the effect of refining the casted structure, and on the contrary, there is a risk that a coarse intermetallic compound which is to be the starting point of fracture may be generated. It is preferable that Ti is added by a rod hardener (Al-Ti-B alloy) during the casting. B added at this time together with Ti as the rod hardener is acceptable.

Other Component Elements

[0033] As long as the effects of the present invention are not impaired, it is permissible to contain other elements.

(2) Structure

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**[0034]** The aluminum alloy plastic working material has a volume ratio of an  $Al_4Ca$  phase, which is a dispersed phase, is 25% or more, the  $Al_4Ca$  phase comprises a tetragonal  $Al_4Ca$  phase and a monoclinic  $Al_4Ca$  phase, and an intensity ratio  $(l_1/l_2)$  of the highest diffraction peak  $(l_1)$  attributed to the tetragonal system to the highest diffraction peak  $(l_2)$  attributed to the monoclinic system, which are obtained by an X-ray diffraction measurement, is 1 or less.

[0035] The tetragonal  $Al_4Ca$  phase and the monoclinic  $Al_4Ca$  phase exist in the  $Al_4Ca$  phase, which is a dispersed phase, and the volume ratio of the combined  $Al_4Ca$  phase is 25% or more. By making the volume ratio of the  $Al_4Ca$  phase to 25% or more, it is possible to impart an excellent proof stress to the aluminum alloy plastic working material. [0036] Further, it is preferable that an average crystal grain size of the  $Al_4Ca$  phase is 1.5  $\mu$ m or less. When the average grain size of the  $Al_4Ca$  phase exceeds 1.5  $\mu$ m, there is a risk that the proof stress of the aluminum alloy plastic working material decreases.

[0037] Though the crystal structure of the  $Al_4Ca$  phase is generally a tetragonal crystal, the present inventors have intensively studied and found that when the monoclinic crystal structure exists in the  $Al_4Ca$  phase, the proof stress do not almost decrease, but the Young's modulus is greatly decreased. It is not necessary that all crystal structure of the  $Al_4Ca$  phases is monoclinic, and it may be in the state of being mixed with the tetragonal crystal. The existence of the  $Al_4Ca$  phase which has the monoclinic crystal structure can be identified, for example, by measuring the diffraction peak with X ray diffraction method.

**[0038]** Regarding the  $AI_4Ca$  phases, the intensity ratio  $(I_1/I_2)$  of the highest diffraction peak  $(I_1)$  attributed to the tetragonal system to the highest diffraction peak  $(I_2)$  attributed to the monoclinic system, can generally be obtained by a X-ray diffraction measurement. The lattice constants of the tetragonal  $AI_4Ca$  are a = 0.4354 and c = 1.118, and the lattice constants of the orthorhombic  $AI_4Ca$  are a = 0.6158, b = 0.6175, c = 1.118,  $\beta = 88.9$ °.

2. Method for Producing Aluminum Alloy Plastic Material

**[0039]** FIG. 1 shows a process chart of the aluminum alloy plastic working material of the present invention. The method for producing the aluminum alloy plastic working material of the present invention includes a first step (S01) of subjecting an aluminum alloy ingot to plastic working, and a second step (S02) of applying a heat treatment. Each step and the like will be explained herein below.

(1) Casting

**[0040]** After subjecting the aluminum alloy molten metal having the composition of the above-mentioned aluminum alloy plastic working material of the present invention to conventionally known molten metal cleaning treatments such as desulfurization treatment, degassing treatment, and filtration treatment, the molten metal is casted into an ingot having a desired shape.

**[0041]** There is no particular restriction on the casting method, and various conventionally known casting methods can be used. For example, it is preferable, by using a continuous casting method such as DC casting, to cast into a shape that the plastic working (extrusion, rolling, forging, etc.) in the first step (S01) is easy to be performed. In the casting, a rod hardener (Al-Ti-B) may be added to improve casting property.

**[0042]** Generally, in the case of preparing an aluminum alloy, before the ingot is subjected to plastic working, a homogenization treatment is carried out where the ingot is held at a temperature of 400 to 600 °C, but when this homogenization treatment is performed, the  $Al_4Ca$  phase tends to be large (average grain size of 1.5  $\mu$ m or larger), and since the proof stress of the aluminum alloy reduces, it is preferable that the homogenization treatment would not be performed in the method for producing aluminum alloy plastic working material according to the present invention.

## (2) First Step (S01)

[0043] The first step (S01) is a step of subjecting the aluminum alloy ingot obtained in (1) to the plastic working to obtain a desired shape.

**[0044]** For the plastic working such as extrusion, rolling, or forging, either hot working or cold working may be used, or a plurality of them may be combined. By performing the plastic working, the aluminum alloy becomes a processed structure, and the proof stress is improved. In the stage of the plastic working, most Al<sub>4</sub>Ca phases contained in the aluminum alloy have the tetragonal crystal structure.

## 10 (3) Second Step (S02)

[0045] The second step (S02) is a step for applying the heat treatment to the aluminum alloy plastic working material obtained in the first step (S01).

**[0046]** By subjecting the aluminum alloy plastic working material subjected to plastic working in the first step (S01) to the heat treatment at 100 to 300 °C, a part of the tetragonal  $Al_4$ Ca phase can be converted into the monoclinic crystal. The change from the tetragonal to the monoclinic is difficult to occur when the holding temperature is less than 100 °C. On the other hand, since, when the holding temperature is 300 °C or higher, recrystallization of the aluminum base material may occur and there is a risk that the proof stress may be reduced, the holding temperature of the heat treatment is preferably 100 to 300 °C, more preferably 160 to 240 °C.

**[0047]** Though the optimum period of time for the heat treatment varies depending on the size and shape of the aluminum alloy plastic working material to be treated, it is preferable that the temperature of at least the aluminum alloy plastic working material is kept at the above holding temperature for 1 hour or more.

**[0048]** The representative embodiments of the present invention have been described above, but the present invention is not limited only to these embodiments, and various design changes are possible, and all such design changes are included in the technical scope of the present invention.

#### **EXAMPLES**

#### «Example»

**[0049]** An aluminum alloy having the composition shown Table 1 was cast into an ingot (billet) of  $\varphi$ 8 inches by a DC casting method without any homogenization treatment, and then, plastic-working at an extrusion temperature of 500 °C to obtain a plate having a width of 180 mm  $\times$  a thickness of 8 mm. Then, after cold rolling to a thickness of 5 mm, a heat treatment was carried out to hold at 200 °C for 4 hours to obtain the present aluminum alloy working plastic material.

[Table 1]

	(unit: wt%)				
	Ca	Fe	Ti	Al	
Present aluminum alloy plastic working material 1 Comparative aluminum alloy plastic working material 1	5.2	0.001	0.002	Bal.	
Present aluminum alloy plastic working material 2 Comparative aluminum alloy plastic working material 2	6.2	0.05	0.002	Bal.	
Present aluminum alloy plastic working material 3 Comparative aluminum alloy plastic working material 3	7.3	0.05	0.01	Bal.	
Present aluminum alloy plastic working material 4 Comparative aluminum alloy plastic working material 4	8.1	0.001	0.01	Bal.	
Present aluminum alloy plastic working material 5 Comparative aluminum alloy plastic working material 5	9.5	0.05	0.05	Bal.	

[0050] The obtained present aluminum alloy plastic working material 3 was subjected to the X-ray diffraction measurement to measure the position pf the peak of the  $Al_4Ca$  phase. In the X-ray diffraction measurement, a specimen of 20 mm  $\times$  20 mm was cut out from the plate-like aluminum alloy plastic working material, the surface layer portion was removed by about 500  $\mu$ m, and then a  $\theta$ -2  $\theta$  measurement was carried out with respect to the region from a Cu-Ka beam

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source. The results are shown in FIG. 2. The intensity ratio  $(I_1/I_2)$  of the highest diffraction peak  $(I_1)$  attributed to the tetragonal system to the highest diffraction peak  $(I_2)$  attributed to the monoclinic system was 0.956.

**[0051]** In addition, JIS-14B specimens were cut out from the present aluminum alloy plastic working materials 1 to 5, and the Young's modulus and proof stress were measured by a tensile test. The obtained results are shown in Table 2. In addition, the volume ratio of the dispersed phase (Al<sub>4</sub>Ca phase) calculated from the structural observation by the optical microscope are shown in Table 2.

[0052] The present aluminum alloy plastic working materials 6 to 9 were obtained in the same manner as in the case of the present aluminum alloy plastic working material 3 except that the heat treatment temperature was any one of 100 °C, 160 °C, 240 °C and 300 °C. In addition, in the same manner as in the case of the present aluminum alloy plastic working materials 1 to 5, the Young's modulus and proof stress were measured by a tensile test. The obtained results are shown in Table 3.

#### <<Comparative Example>>

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[0053] An aluminum alloy having the composition shown Table 1 was cast into an ingot (billet) of  $\varphi 8$  inches by a DC casting method without any homogenization treatment, and then, plastic-working at an extrusion temperature of 500 °C to obtain a plate having a width of 180 mm  $\times$  a thickness of 8 mm. Thereafter, the cold rolling to a thickness of 5 mm was carried out to obtain the comparative aluminum alloy plastic working materials 1 to 5.

[0054] The obtained comparative aluminum alloy plastic working material 3 was subjected to the X-ray diffraction measurement to measure the position pf the peak of the Al<sub>4</sub>Ca phase. In the X-ray diffraction measurement, a specimen of 20 mm  $\times$  20 mm was cut out from the plate-like aluminum alloy plastic working material, the surface layer portion was removed by about 500  $\mu$ m, and then a  $\theta$ -2  $\theta$  measurement was carried out with respect to the region from a Cu-Ka beam source. The results are shown in FIG. 2. The intensity ratio (I<sub>1</sub>/I<sub>2</sub>) of the highest diffraction peak (I<sub>1</sub>) attributed to the tetragonal system to the highest diffraction peak (I<sub>2</sub>) attributed to the monoclinic system was 1.375.

[0055] In addition, JIS-14B specimens were cut out from the comparative aluminum alloy plastic working materials 1 to 5, and the Young's modulus and proof stress were measured by a tensile test. The obtained results are shown in Table 2. [0056] The comparative aluminum alloy plastic working materials 6 and 7 were obtained in the same manner as in the case of the present aluminum alloy plastic working material 3 except that the heat treatment temperature was 90 °C and 310 °C. In addition, in the same manner as in the case of the comparative aluminum alloy plastic working materials 1 to 5, the Young's modulus and proof stress were measured by a tensile test. The obtained results are shown in Table 3. [0057] The comparative aluminum alloy plastic working material 8 was obtained in the same manner as in the case of the present aluminum alloy plastic working material 3 except that, after casting in an ingot (billet), the homogenization treatment was carried out while holding at 550 °C. In addition, JIS-14B specimen was cut out from the comparative aluminum alloy plastic working material 8, and the Young's modulus and proof stress were measured by a tensile test. The obtained results are shown in Table 4. The Young's modulus and the proof stress of the present aluminum alloy plastic working material 3 which is different only in the presence or absence of homogenization treatment are also shown as comparison data.

## [Table 2]

[Table 2]					
	Heat treatment	Volume ratio of dispersed phase (%)	Young's modulus (GPa)	Proof stress (MPa)	Tensile strength (MPa)
Present aluminum alloy plastic working material 1		26.7	58	147	245
Present aluminum alloy plastic working material 2		31.2		167	258
Present aluminum alloy plastic working material 3	Did	35.9	53	169	254
Present aluminum alloy plastic working material 4		39.9	51	208	272
Present aluminum alloy plastic working material 5		44.3	48	173	269

(continued)

5		Heat treatment	Volume ratio of dispersed phase (%)	Young's modulus (GPa)	Proof stress (MPa)	Tensile strength (MPa)
	Comparative aluminum alloy plastic working material 1		-	67	176	259
10	Comparative aluminum alloy plastic working material 2	Non	-	64	184	268
	Comparative aluminum alloy plastic working material 3		-	61	189	265
15	Comparative aluminum alloy plastic working material 4		-	57	222	285
	Comparative aluminum alloy plastic working material 5		-	56	186	276

[0058] From the results shown in Table 2, when comparing the present aluminum alloy plastic working material having the same composition with the comparative aluminum alloy plastic working material, the Young's modulus of the aluminum alloy plastic working materials of the present invention (the present aluminum alloy plastic working materials 1 to 5) are greatly lower than the Young's modulus of the comparative aluminum alloy plastic working materials 1 to 5 which were not subjected to the heat treatment. On the other hand, the proof stress and tensile strength of the present aluminum alloy plastic working materials 1 to 5 are not greatly reduced as compared with the comparative aluminum alloy plastic working materials 1 to 5. It is clear that the volume ratios of the dispersed phase (Al<sub>4</sub>Ca phase) in the aluminum alloy plastic working materials of the present invention are 25% or more.

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[Table 3]

	Heat treatment temperature (°C)	Young's modulus (GPa)	Proof stress (MPa)	Tensile strength (MPa)
Present aluminum alloy plastic working material 6	100	54	187	267
Present aluminum alloy plastic working material 7	160	54	172	262
Present aluminum alloy plastic working material 8	240	53	167	252
Present aluminum alloy plastic working material 9	300	52	161	240
Comparative aluminum alloy plastic working material 6	90	59	195	275
Comparative aluminum alloy plastic working material 7	310	53	143	231

**[0059]** From the results shown in Table 3, when the holding temperature of the heat treatment is 90 °C (comparative aluminum alloy plastic working material 6), the Young's modulus shows a high value (almost not lowered). In addition, when the holding temperature of the heat treatment is 310 °C (comparative aluminum alloy plastic working material 7), though the Young's modulus is lowered, the proof stress and tensile strength are simultaneously lowered. From the results, when the holding temperature of the heat treatment was 310 °C, it is considered that the recrystallization of the plastic working structure progressed.

[0060] The structural photographs of the present aluminum alloy plastic working material 3 and the comparative aluminum alloy plastic working material 8 by an optical microscope are shown in FIG. 3 and FIG. 4, respectively. In the structure photograph, the black region is the  $Al_4Ca$  phase, and the average crystal grain size of the  $Al_4Ca$  phase is

measured by image analysis. The obtained results are shown in Table 4.

#### [Table 4]

	Homogenization treatment	Average crystal grain size of Al <sub>4</sub> Ca phase (μm)	Young's modulus (GPa)	Proof stress (MPa)	Tensile strength (MPa)
Comparative aluminum alloy plastic working material 8	Did	1.56	53	158	229
Present aluminum alloy plastic working material 3	Non	1.15	53	169	254

[0061] From the results shown in Table 4, when subjecting to the homogenization treatment maintained at 550 °C (comparative aluminum alloy plastic working material 8), it is recognized that the proof stress and the tensile strength are reduced. Here, the average crystal grain size of the Al<sub>4</sub>Ca phase is increased by the homogenization treatment to 1.56 μm. It is considered that the proof stress and the tensile strength are reduced due to the increase in the average crystal grain size.

#### Claims

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1. An aluminum alloy plastic working material, which comprises:

5.0 to 10.0 wt% of Ca, and

the remainder aluminum and unavoidable impurities,

a volume ratio of an Al<sub>4</sub>Ca phase, which is a dispersed phase, is 25% or more,

the Al<sub>4</sub>Ca phase comprises a tetragonal Al<sub>4</sub>Ca phase and a monoclinic Al<sub>4</sub>Ca phase, and

an intensity ratio  $(I_1/I_2)$  of the highest diffraction peak  $(I_1)$  attributed to the tetragonal system to the highest diffraction peak  $(I_2)$  attributed to the monoclinic system, which are obtained by an X-ray diffraction measurement, is 1 or less.

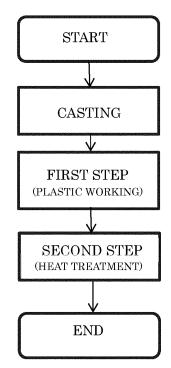
- 2. The aluminum alloy plastic working material according to claim 1, further comprising at least one or more of Fe: 0.05 to 1.0 wt% and Ti: 0.005 to 0.05 wt%.
- 3. The aluminum alloy plastic working material according to claim 1 or 2, wherein an average crystal grain size of the  $Al_{\Delta}Ca$  phase is 1.5  $\mu$ m or less.
- 40 **4.** A method for producing an aluminum alloy plastic working material, comprising:

a first step for obtaining a plastic workpiece of an aluminum alloy by subjecting an aluminum alloy ingot which contains 5.0 to 10.0 wt% of Ca with the remainder aluminum and inevitable impurities, and has a volume ratio of an  $Al_4Ca$  phase which is a dispersed phase of 25% or more to a plastic processing, and a second step for subjecting to a heat treatment in a temperature range of 100 to 300 °C.

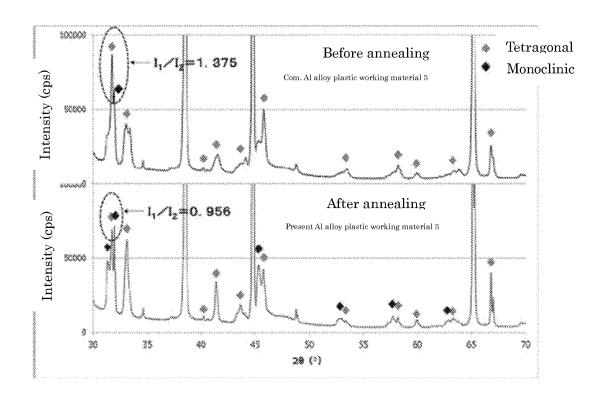
- 5. The method for producing an aluminum alloy plastic working material according to claim 4, wherein aluminum alloy ingot contains at least one or more of Fe: 0.05 to 1.0 wt% and Ti: 0.005 to 0.05 wt%.
- 6. The method for producing an aluminum alloy plastic working material according to claim 4 or 5, wherein, before the first step, the aluminum alloy ingot is not subjected to a heat treatment where the ingot is maintained at a temperature of 400 °C or more.

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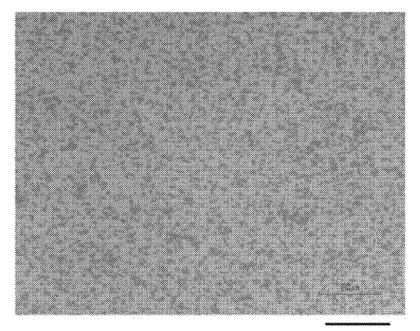
[FIG. 1]



[FIG. 2]

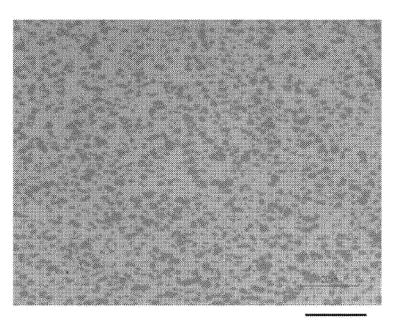


[FIG. 3]



20µm

# [FIG. 4]



20µm

#### INTERNATIONAL SEARCH REPORT International application No. PCT/JP2017/024184 A. CLASSIFICATION OF SUBJECT MATTER 5 C22C21/00(2006.01)i, C22F1/04(2006.01)i, C22F1/00(2006.01)n According to International Patent Classification (IPC) or to both national classification and IPC FIELDS SEARCHED 10 Minimum documentation searched (classification system followed by classification symbols) C22C21/00-21/18, C22F1/00-3/02 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched 1922-1996 Jitsuyo Shinan Toroku Koho Jitsuvo Shinan Koho 15 Kokai Jitsuyo Shinan Koho 1971-2017 Toroku Jitsuyo Shinan Koho Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) JSTPlus(JDreamIII), Science Direct 20 DOCUMENTS CONSIDERED TO BE RELEVANT Category\* Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. Α JP 2011-105982 A (Nissan Motor Co., Ltd.), 1-6 02 June 2011 (02.06.2011), (Family: none) 25 JP 2010-126740 A (Nissan Motor Co., Ltd.), Α 1 - 610 June 2010 (10.06.2010), (Family: none) WO 2009/035029 A1 (Nissan Motor Co., Ltd.), Α 1-6 30 19 March 2009 (19.03.2009), & EP 2189548 A1 & US 2010/0172792 A1 & CN 101796206 A PELLEGRINI, G et al., Growth and 1-6 Α Crystallography of the Unidirectionally 35 Solidified Al-Al $_4$ Ca Eutectic, Materials Science and Engineering, 1978.02, vol. 34, p. 171-181 Further documents are listed in the continuation of Box C. See patent family annex. 40 Special categories of cited documents: later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) step when the document is taken alone "L" 45 document of particular relevance; the claimed invention cannot be document of parterial recyalic, the cannot 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 "O" document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed "P' document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 50 15 August 2017 (15.08.17) 29 August 2017 (29.08.17) Name and mailing address of the ISA/ Authorized officer Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan Telephone No. 55

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## REFERENCES CITED IN THE DESCRIPTION

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# Patent documents cited in the description

• JP 2011105982 A [0004] [0006]