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(54) **MAGNESIUM ALLOY FOR CASTING AND MAGNESIUM-ALLOY CAST PRODUCT**

(75) Inventors: **Yuki Okamoto**, Aichi-ken (JP); **Kyoichi Kinoshita**, Aichi-ken (JP); **Motoharu Tanizawa**, Aichi-ken (JP); **Kazuhiko Yoshida**, Aichi-ken (JP)

Correspondence Address:
Locke Lord Bissell & Liddell LLP
Attn: IP Docketing
Three World Financial Center
New York, NY 10281-2101 (US)

(73) Assignee: **KABUSHIKI KAISHA TOYOTA JIDOSHOKKI**, Aichi-ken (JP)

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(57) **ABSTRACT**

A magnesium alloy for casting according to the present invention is characterized in that, when the entirety is taken as 100% by mass, it includes copper (Cu) in an amount of from 1% by mass or more to 5% by mass or less, calcium (Ca) in an amount of from 0.1% by mass or more to 5% by mass or less, silver (Ag) in an amount of from 0.1% by mass or more to 5% by mass or less, and the balance comprising magnesium (Mg) and inevitable impurities.

By means of including Cu and Ca, crystallized substances of Mg—Ca compounds crystallize in crystalline grain boundaries between Mg crystalline grains as three-dimensionally mesh shapes, along with Mg—Cu compounds. By means of the three-dimensionally mesh constructions, grain-boundary sliding, which becomes active especially when becoming high temperature, is suppressed, and thereby high-temperature strength and creep resistance at high temperature improve. Moreover, by means of the Ag addition, the Mg crystalline grains become micro-fine and thereby the three-dimensionally mesh constructions, whose continuities are high and which are fine, are formed. In addition, it is less likely that Ag affects the heat conductivity of magnesium alloy adversely.

Fig.1

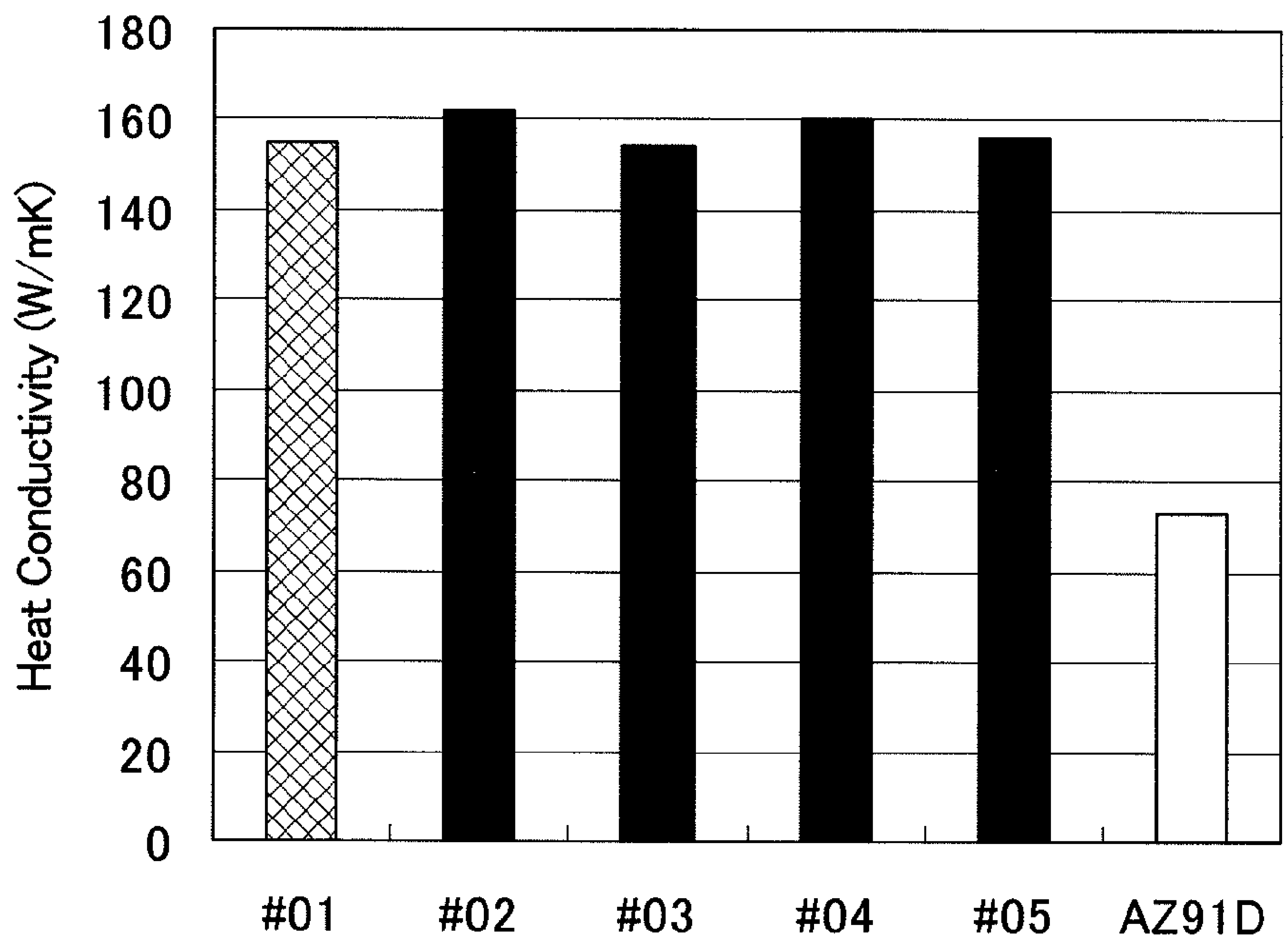
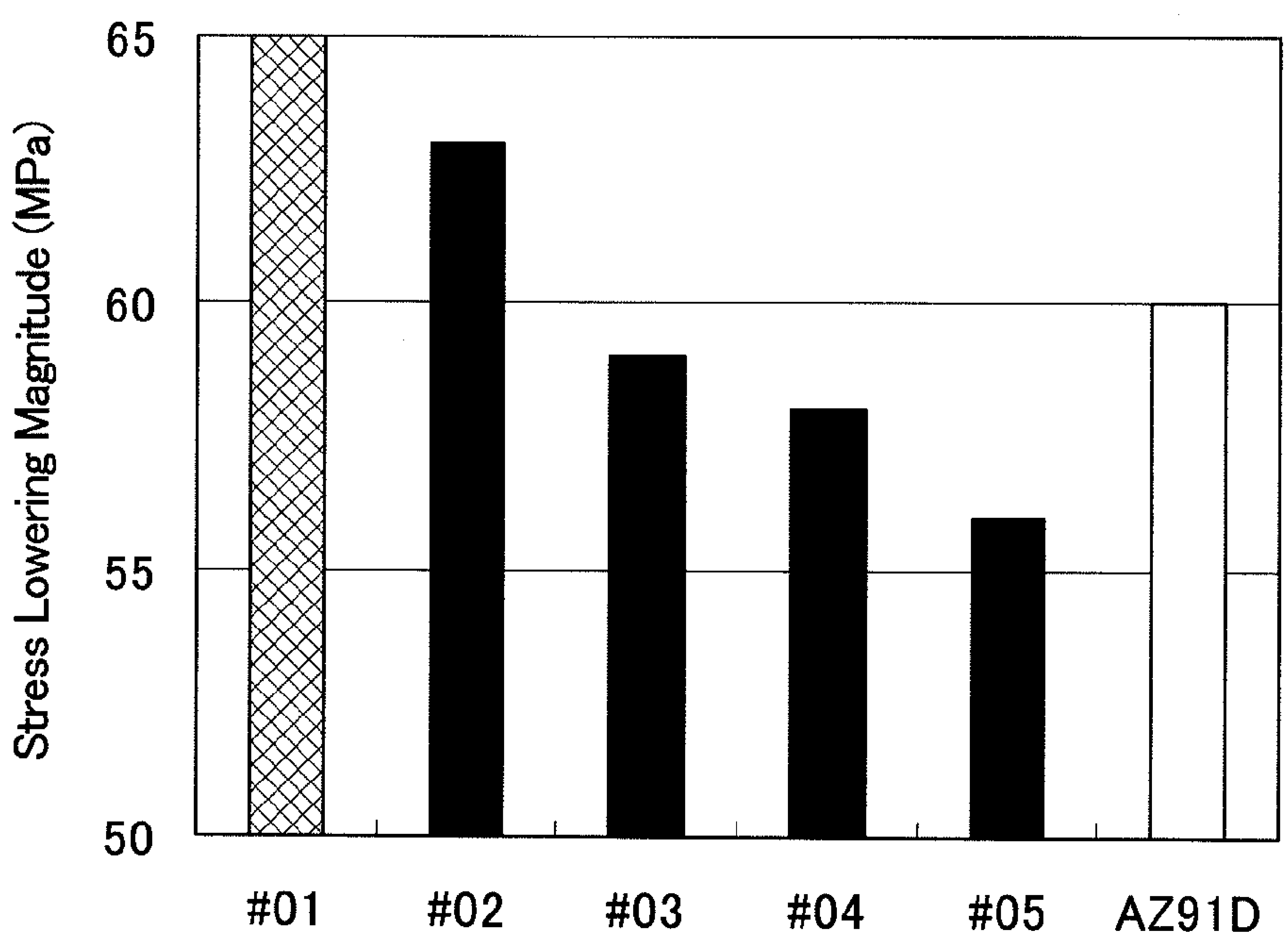

Heat Conductivity (W/mK)
180
160
140
120
100
80
60
40
20
0
#01
#02
#03
#04
#05
AZ91D

Fig.2


Stress Lowering Magnitude (MPa)
65
60
55
50
#01
#02
#03
#04
#05
AZ91D

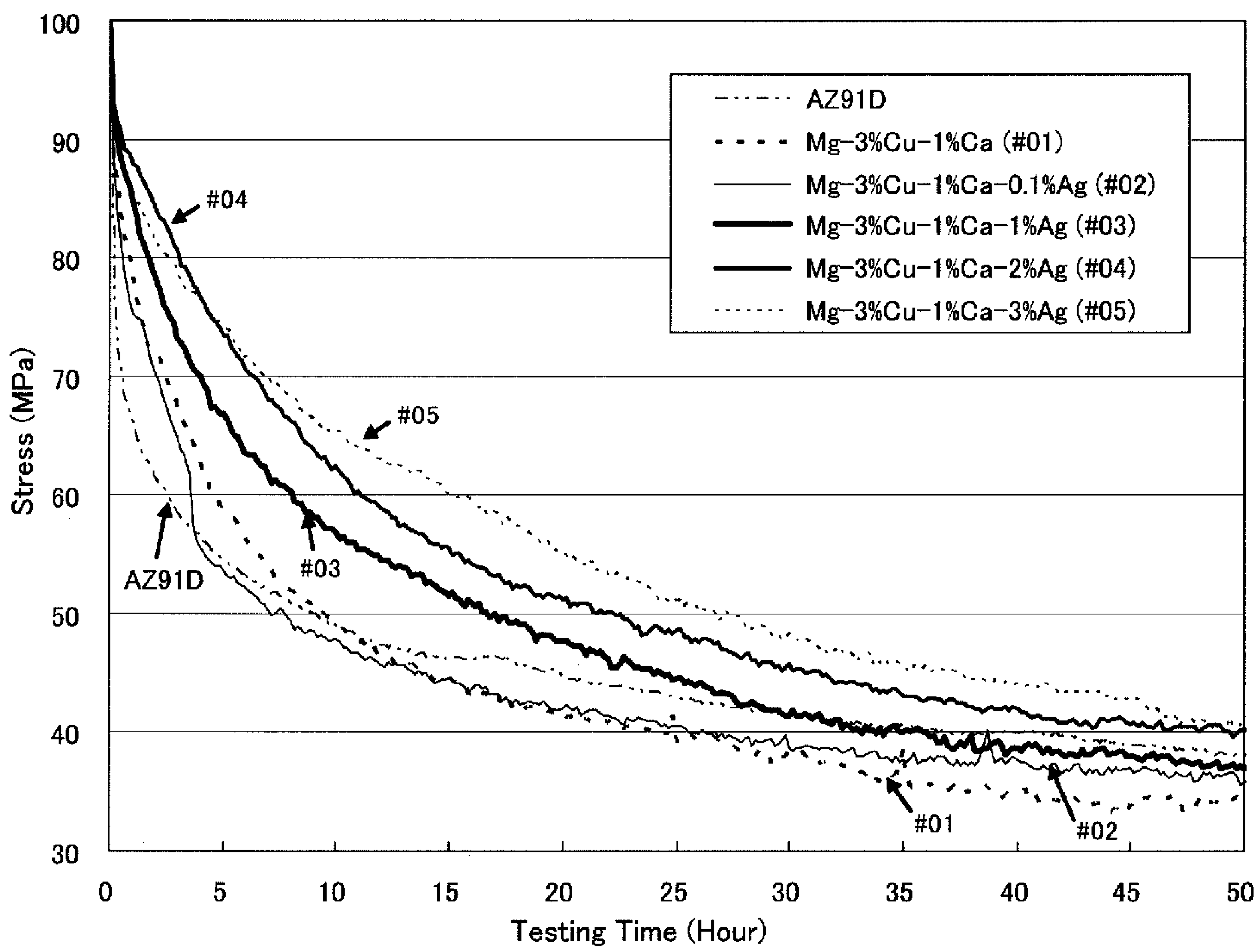

AZ91D
Mg-3%Cu-1%Ca (#01)
Mg-3%Cu-1%Ca-0.1%Ag (#02)
Mg-3%Cu-1%Ca-1%Ag (#03)
Mg-3%Cu-1%Ca-2%Ag (#04)
Mg-3%Cu-1%Ca-3%Ag (#05)
#04
#05
#03
AZ91D
#01
#02
Stress (MPa)
Testing Time (Hour)
100
90
80
70
60
50
40
30
0
5
10
15
20
25
30
35
40
45
50

Fig.3

Fig.4A

(a) #01 : Mg-3%Cu-1%Ca

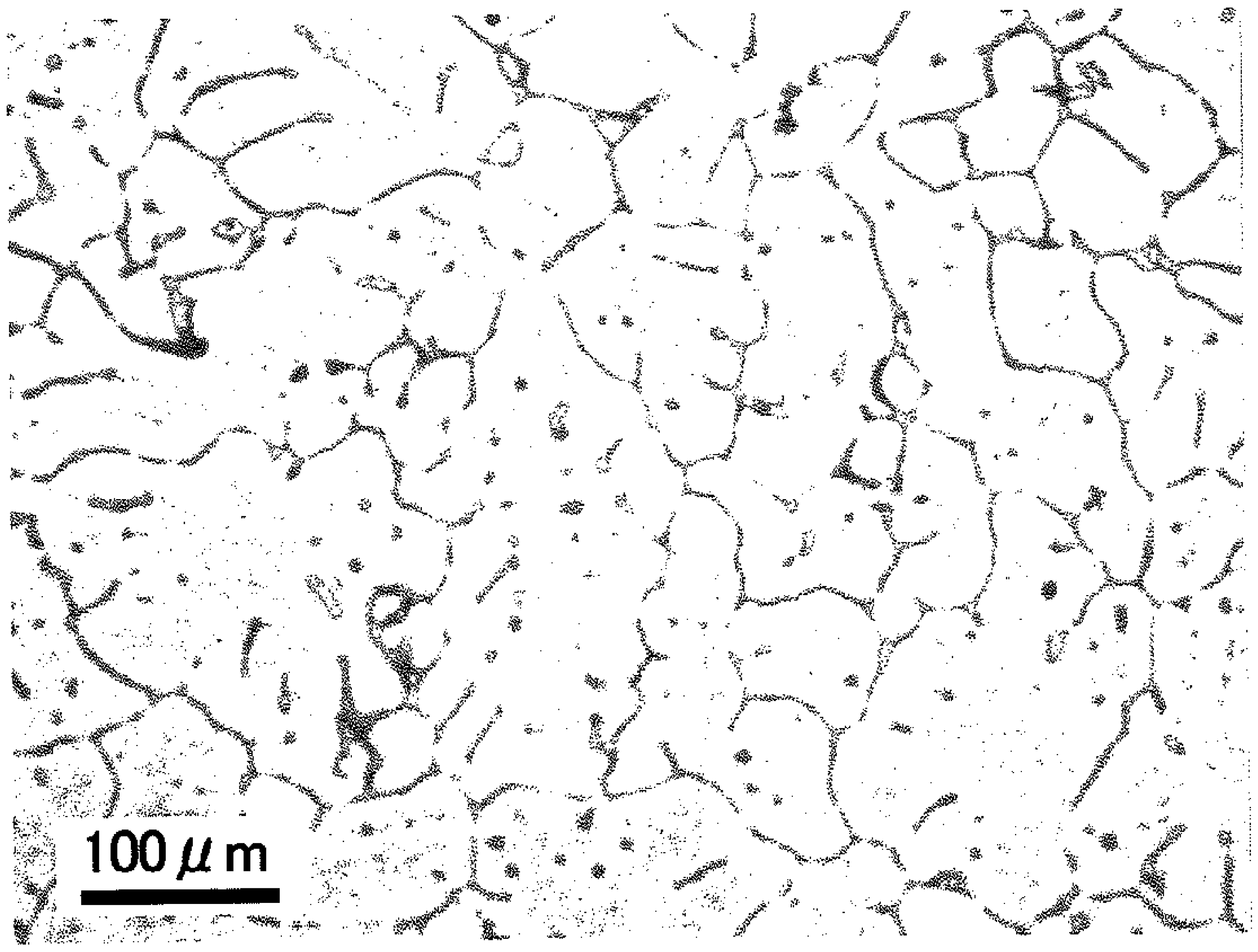


Fig.4B

(b) #01 : Mg-3%Cu-1%Ca

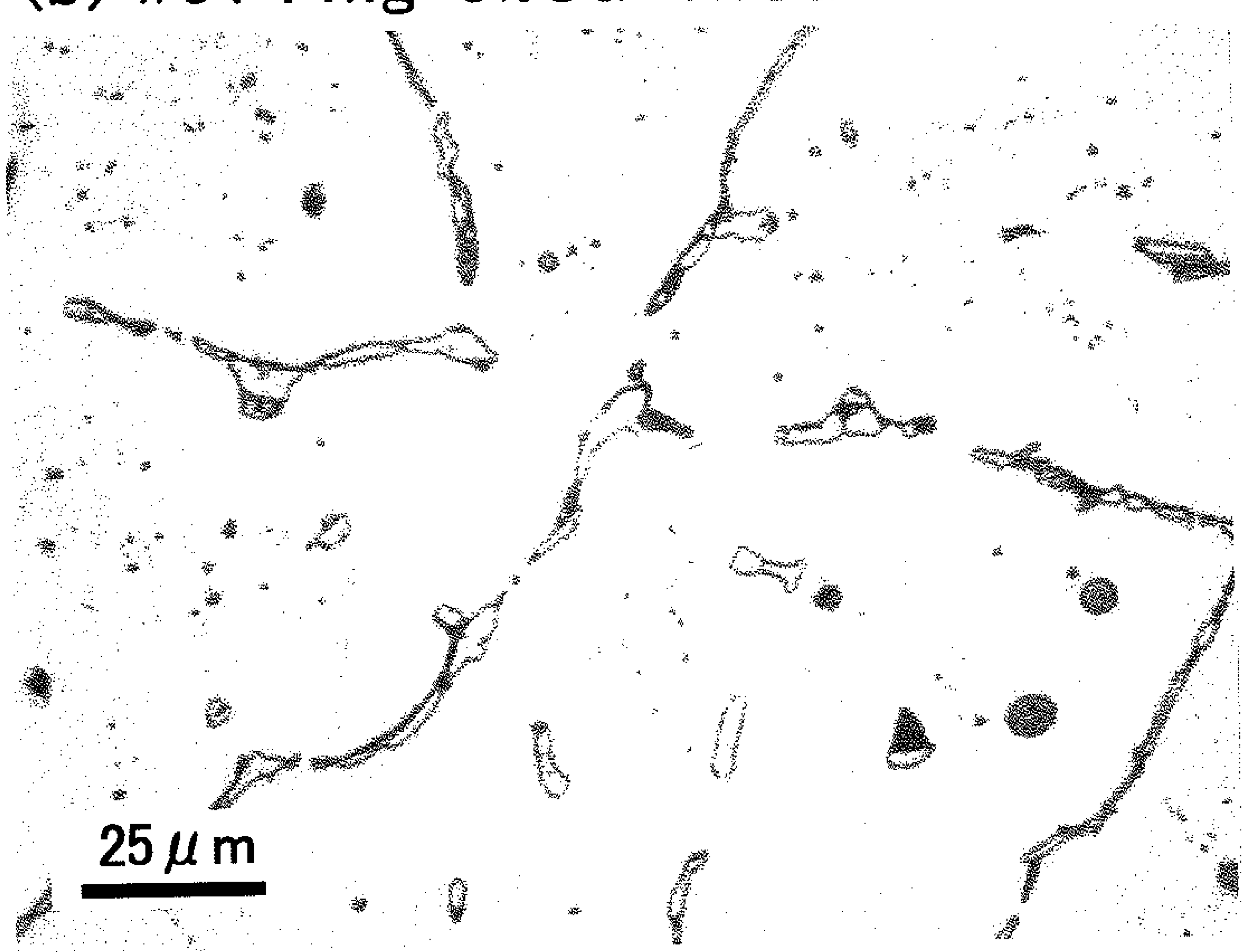


Fig.5A

(a) #02 : Mg-3%Cu-1%Ca-0.1%Ag

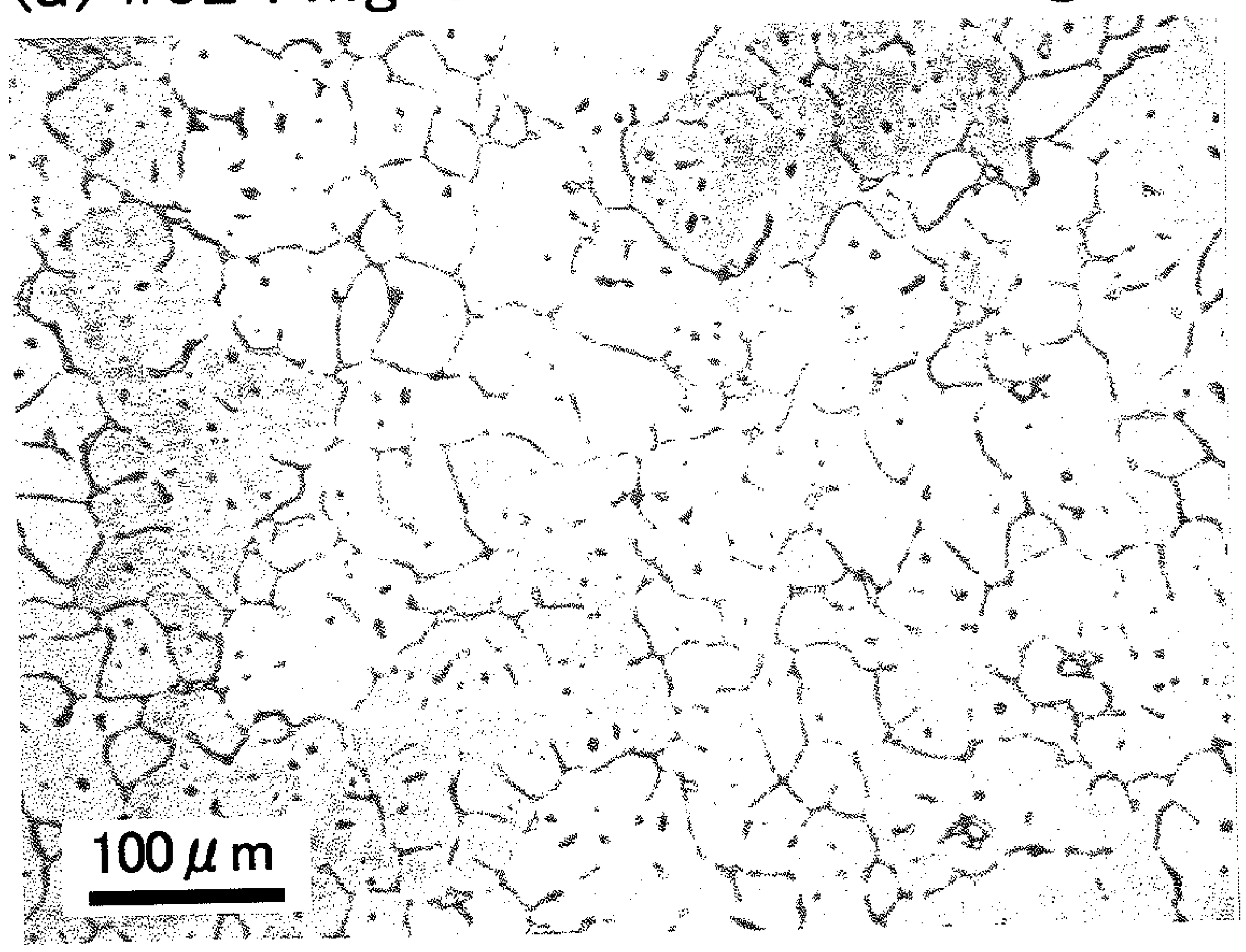


Fig.5B

(b) #02 : Mg-3%Cu-1%Ca-0.1%Ag

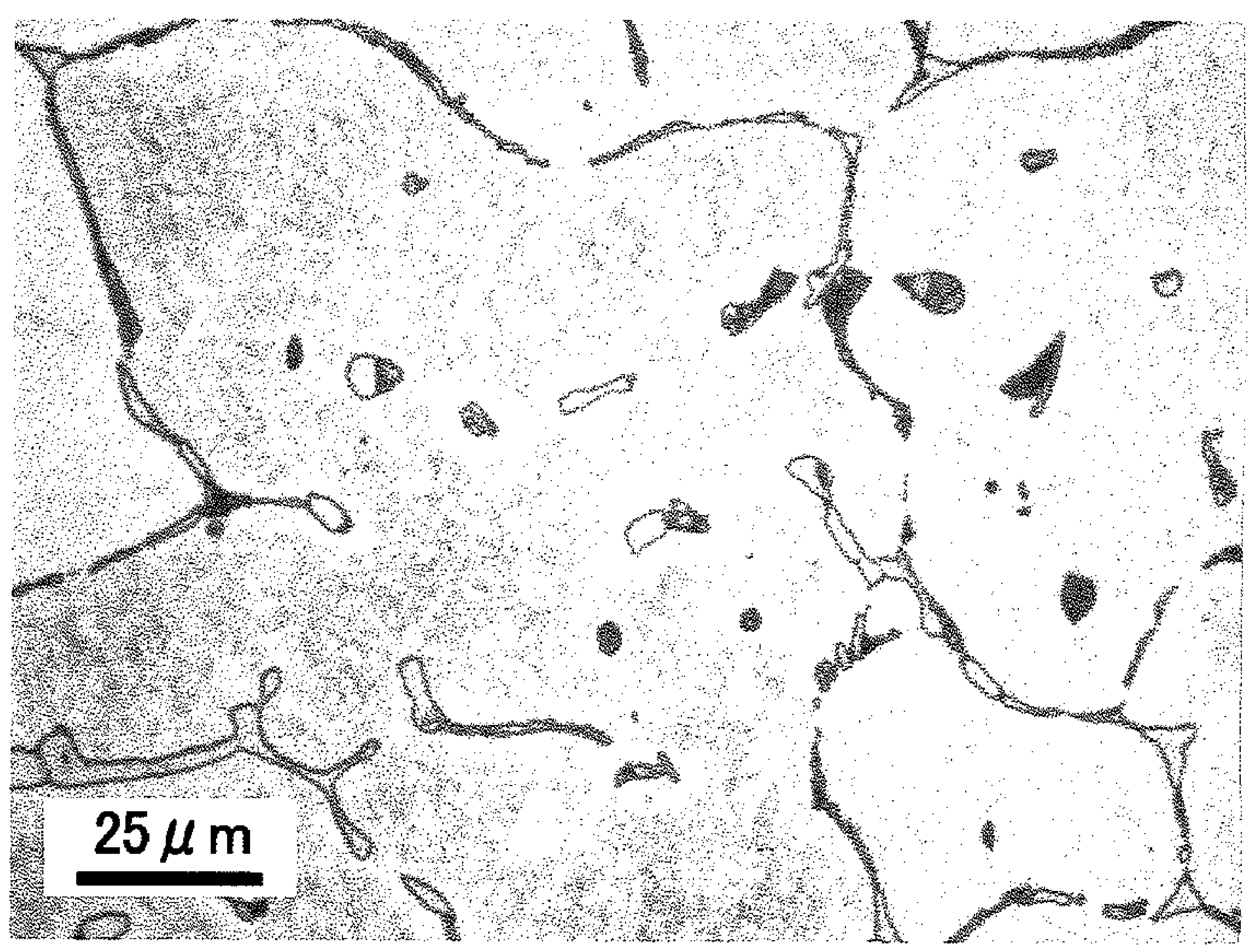


Fig.6A

(a) #03 : Mg-3%Cu-1%Ca-1%Ag

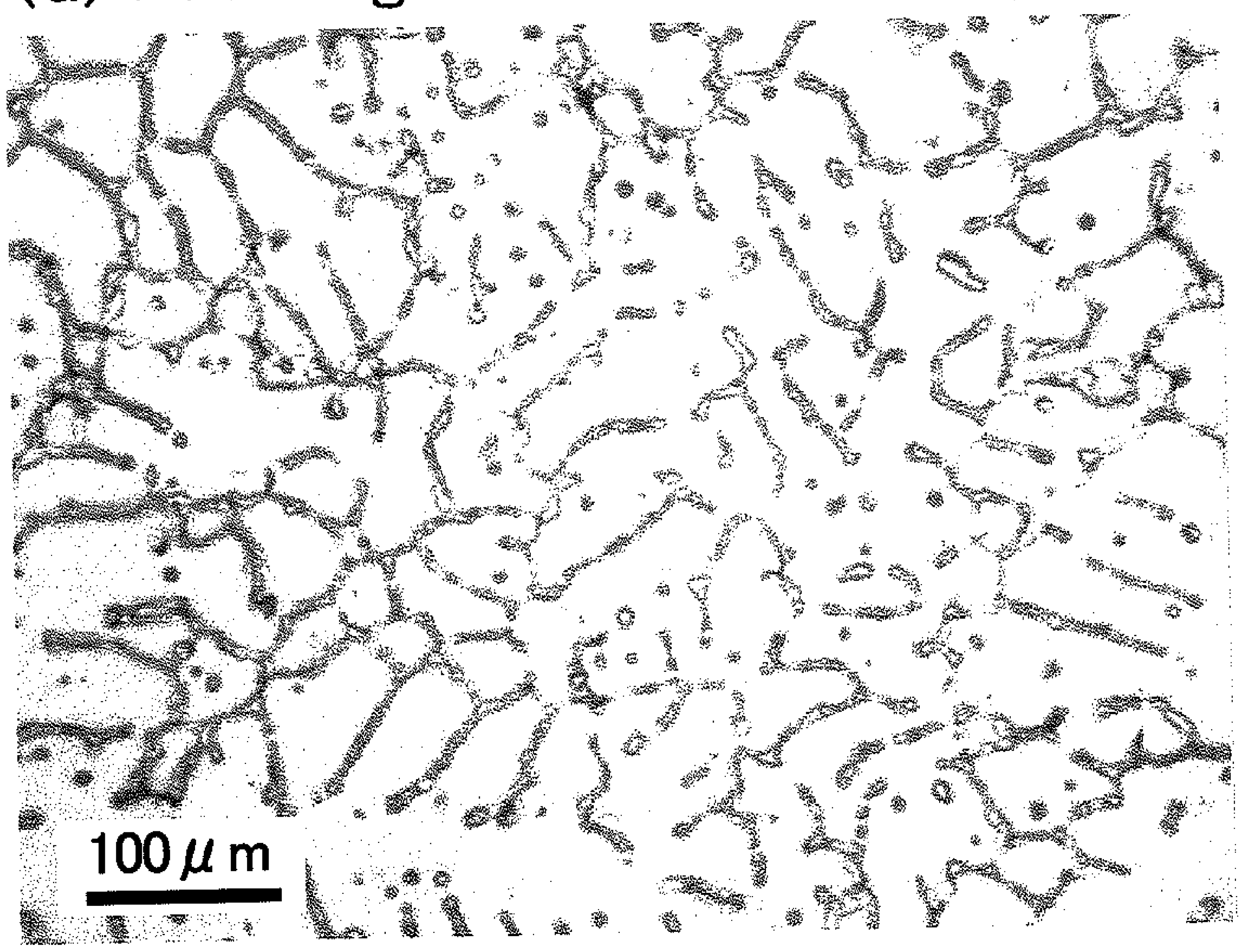


Fig.6B

(b) #03 : Mg-3%Cu-1%Ca-1%Ag

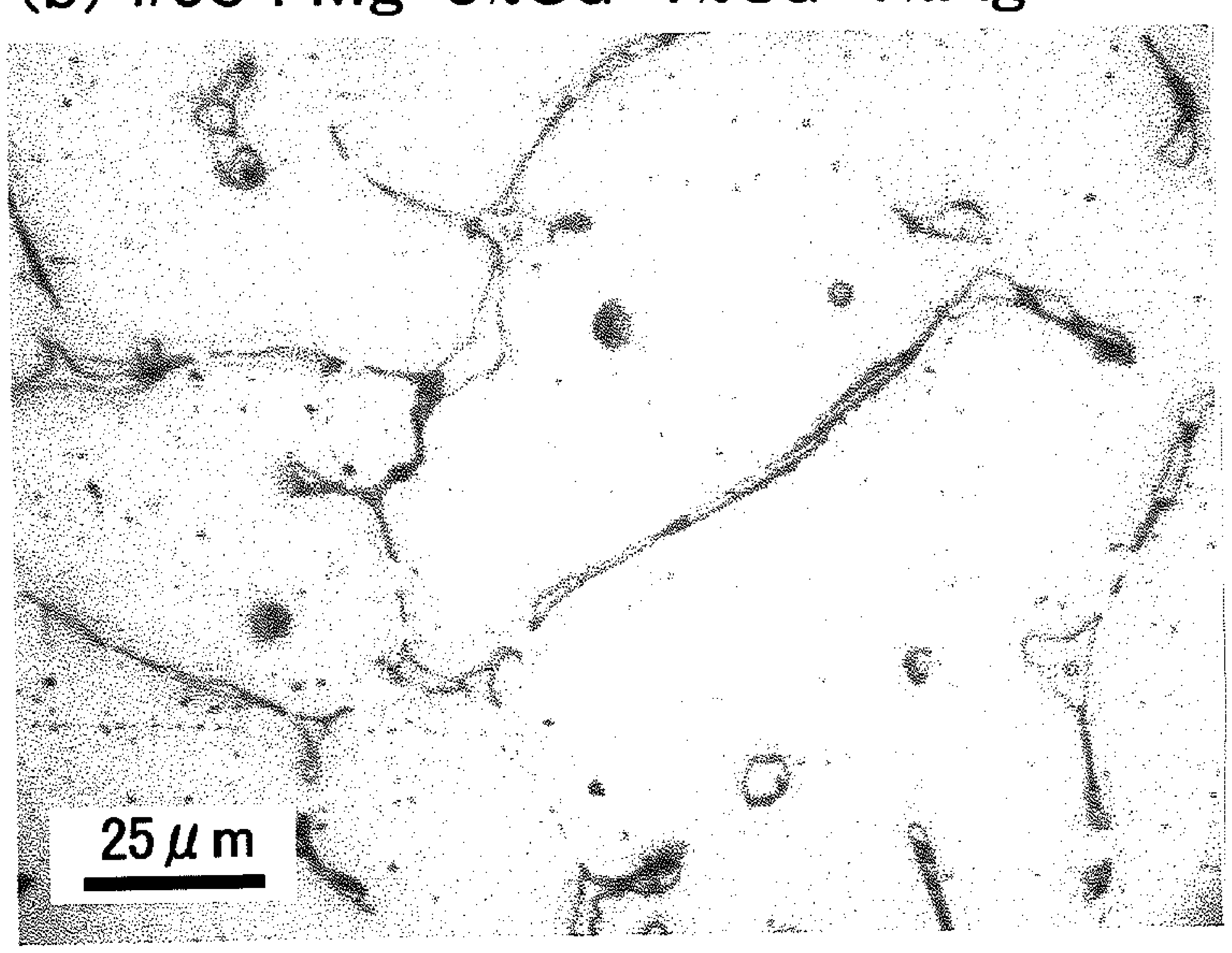


Fig.7A

(a) #04 : Mg-3%Cu-1%Ca-2%Ag

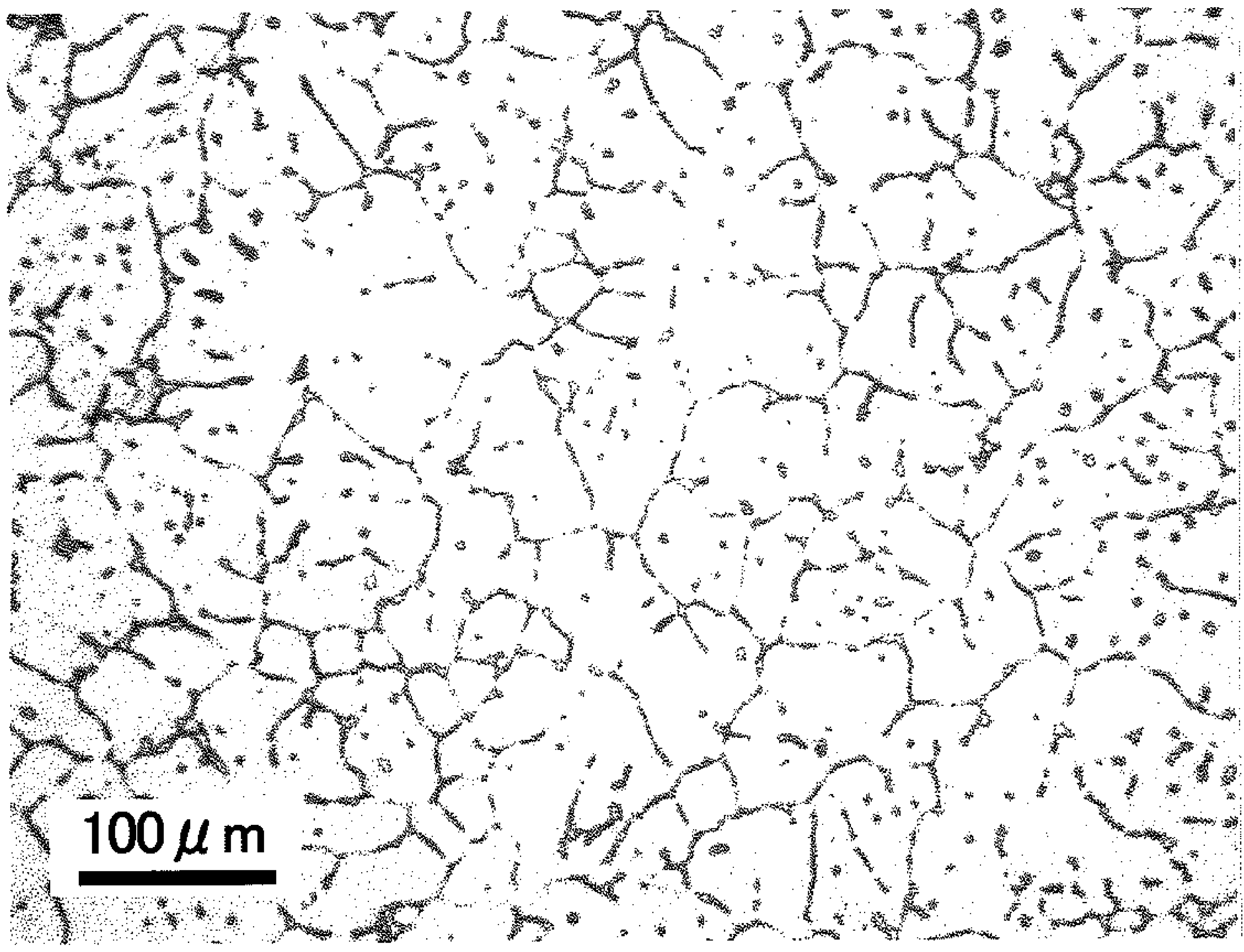


Fig.7B

(b) #04 : Mg-3%Cu-1%Ca-2%Ag

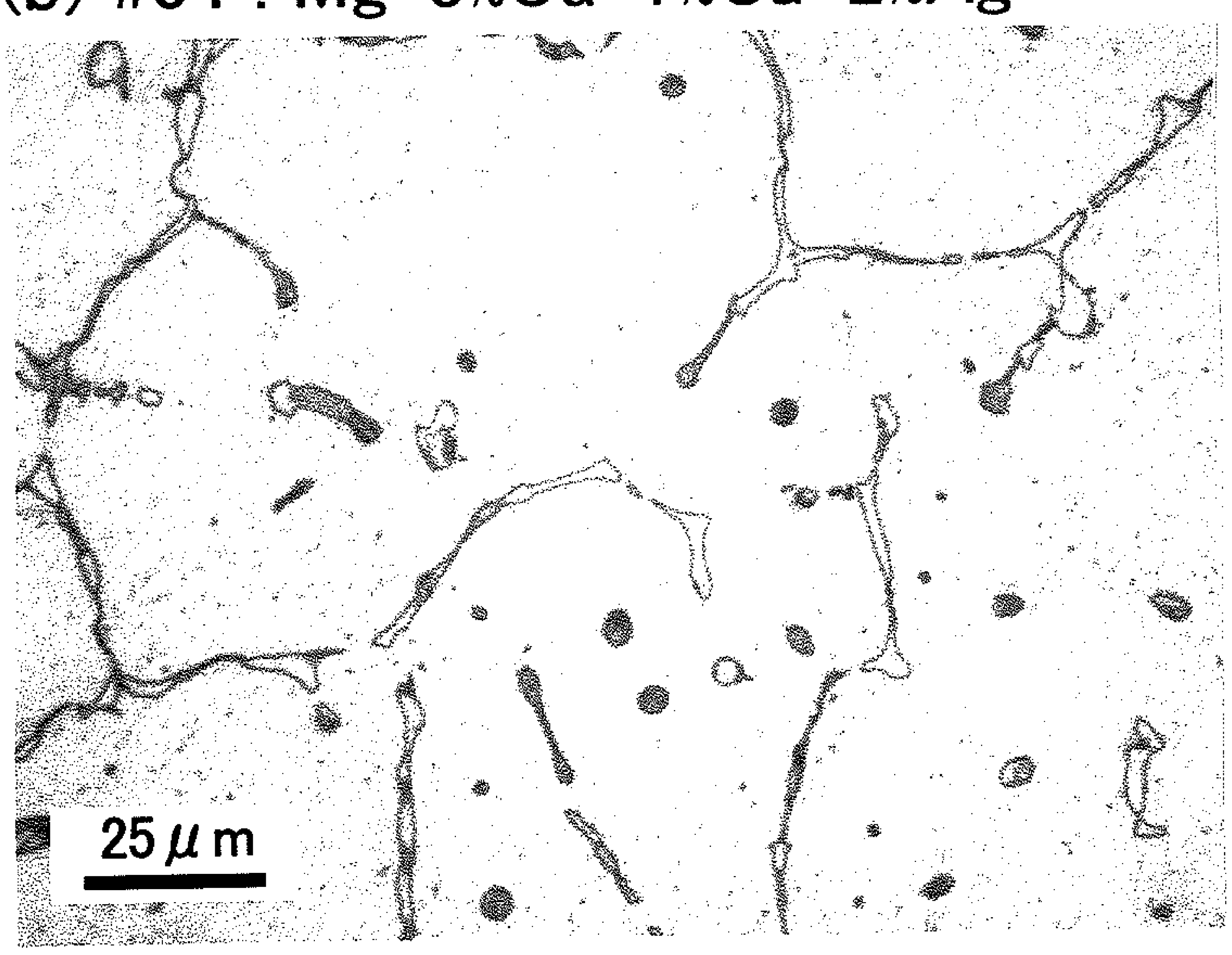


Fig.8A

(a) #05 : Mg-3%Cu-1%Ca-3%Ag

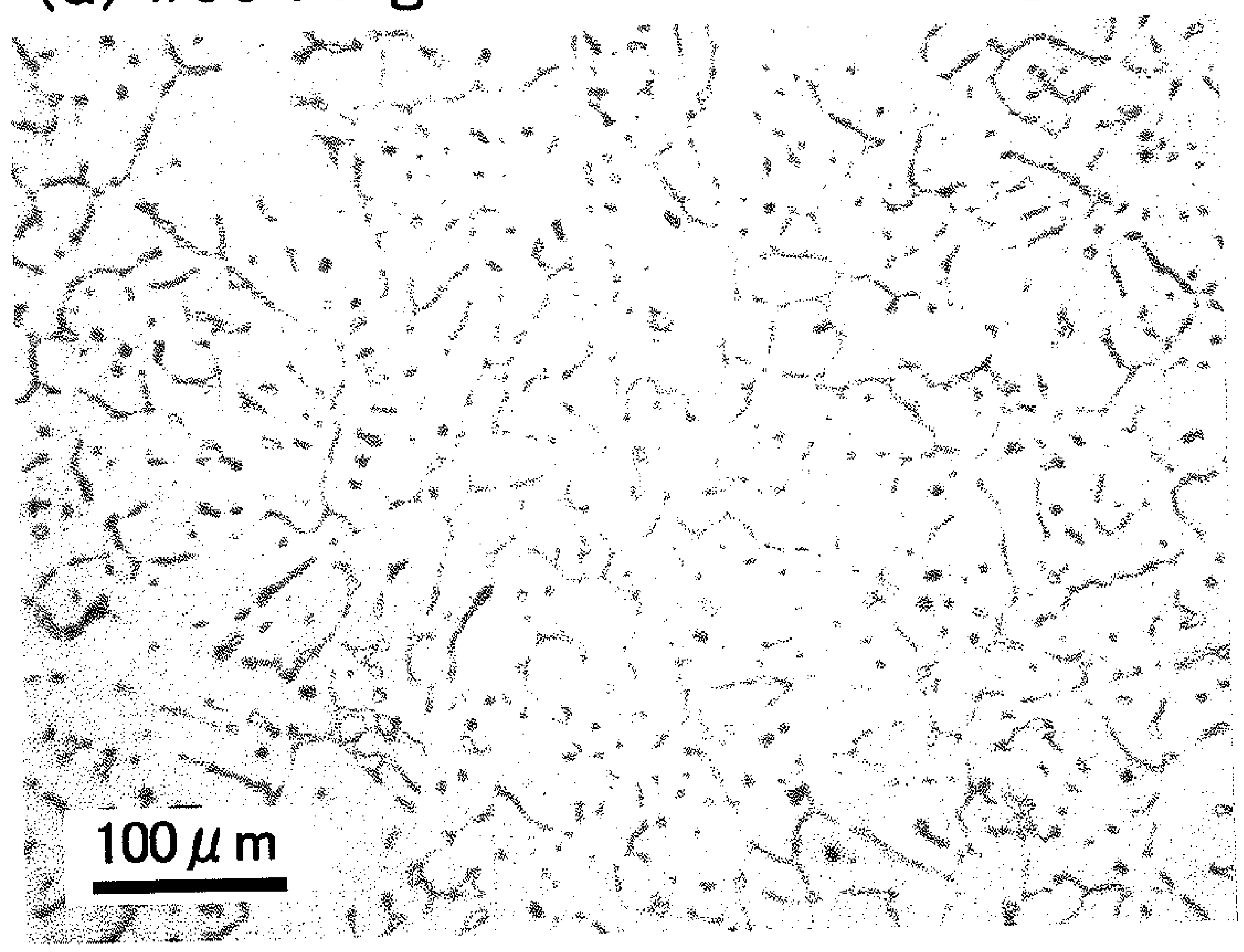
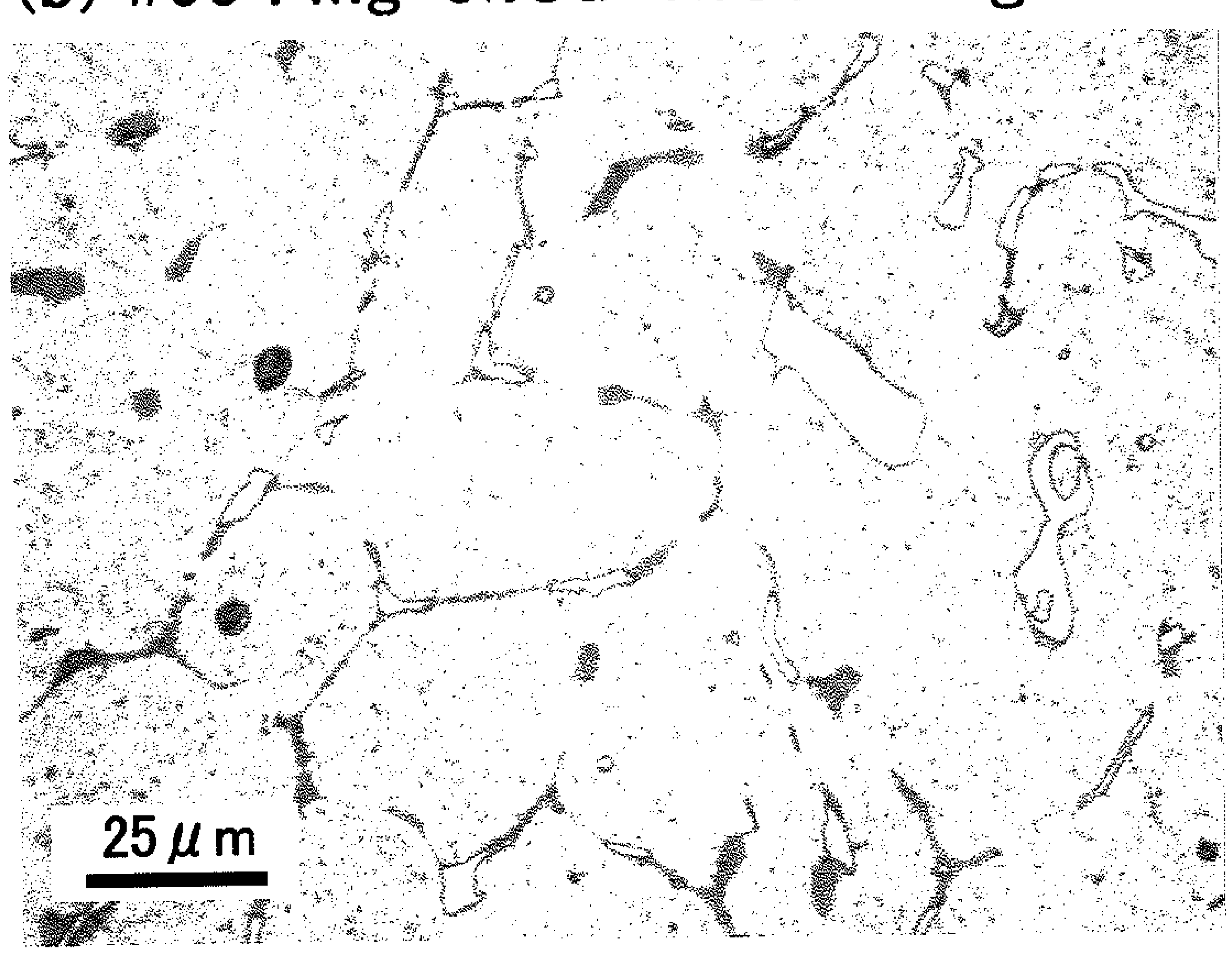


Fig.8B

(b) #05 : Mg-3%Cu-1%Ca-3%Ag



MAGNESIUM ALLOY FOR CASTING AND MAGNESIUM-ALLOY CAST PRODUCT

TECHNICAL FIELD

[0001] The present invention is one which relates to a magnesium alloy for casing, magnesium alloy which is suitable for service under high temperature.

BACKGROUND ART

[0002] Magnesium alloy, which is much more lightweight than aluminum alloy is, is about to come to be used widely for aircraft material, vehicle material, and the like, from the viewpoint of weight saving. However, in magnesium alloy, since the strength and heat resistance are not sufficient depending on applications, further improvement of the characteristics has been sought.

[0003] For example, as a general magnesium alloy, AZ91D (ASTM code) is present, for instance. Since the heat conductivity of AZ91D is 73 W/mK approximately, when it is used in member whose service environment is high temperature, or in member that generates heat in service, the radiation of heat cannot be carried out satisfactorily, and thereby thermal deformation might occur in the member. In particular, when a magnesium alloy whose heat conductivity is low is used as a magnesium alloy that is used in a cylinder head or cylinder block of internal combustion engine, the cylinder head undergoes thermal deformation, or heat dwells within the cylinder block so that the cylinder bores deform, and thereby adverse affects, such as increased friction and declined air tightness, occur. Consequently, a magnesium alloy has been sought, magnesium alloy in which the radiation of heat is carried out satisfactorily by possessing a high heat conductivity, and magnesium alloy which is thereby suitable for usage under high temperature.

[0004] For example, the heat conductivity of a magnesium alloy that has an alloy composition of Mg-3% Cu-1% Ca (the units being "% by mass") is higher than the heat conductivity of AZ91D, because Cu whose heat conductivity is high is included. However, there might be a case where the creep resistance at high temperature is not sufficient, depending on service conditions.

[0005] In Japanese Unexamined Patent Publication (KOKAI) Gazette No. 6-25,791, a magnesium alloy is disclosed, magnesium alloy which includes calcium (Ca) in an amount of 0.8-5% by mass, copper (Cu) in an amount of 0-10% by mass, and zinc (Zn) in an amount of 3-8% by mass. Although the magnesium alloy set forth in Japanese Unexamined Patent Publication (KOKAI) Gazette No. 6-25,791 exhibits high strength at room temperature and high temperature, nothing is set forth on the heat conductivity, and accordingly it is unclear whether the addition of zinc influences the heat conductivity of magnesium alloy or not.

DISCLOSURE OF THE INVENTION

[0006] In view of the aforementioned problematic issues, it is an object for the present invention to provide a magnesium alloy for casting, magnesium alloy which is suitable for usage under high temperature. Moreover, it is an object to provide a cast product, which comprises that magnesium alloy for casting.

[0007] As a result of wholehearted studies, the present inventors found out that it is possible to improve the creep resistance of magnesium alloy at high temperature by adding silver along with copper and calcium as another alloying element of the magnesium alloy, without ever affecting the heat conductivity adversely, and then arrived at completing the present invention based on this.

[0008] Specifically, a magnesium alloy for casting according to the present invention is characterized in that, when the entirety is taken as 100% by mass, it includes:

[0009] copper (Cu) in an amount of from 1% by mass or more to 5% by mass or less;

[0010] calcium (Ca) in an amount of from 0.1% by mass or more to 5% by mass or less;

[0011] silver (Ag) in an amount of from 0.1% by mass or more to 5% by mass or less; and

[0012] the balance comprising magnesium (Mg) and inevitable impurities.

[0013] Since the magnesium alloy for casting according to the present invention includes Cu and Ca, crystallized substances of Mg—Ca compounds crystallize in crystalline grain boundaries between Mg crystalline grains as network shapes (three-dimensionally mesh shapes), along with Mg—Cu compounds. By means of the three-dimensionally mesh constructions, grain-boundary sliding, which becomes active especially when becoming high temperature, is suppressed, and thereby high-temperature strength and creep resistance at high temperature improve.

[0014] Further, since the magnesium alloy for casting according to the present invention includes Ag along with Cu and Ca, the Mg crystalline grains become micro-fine and thereby the three-dimensionally mesh constructions, whose continuities are high and which are fine, are formed. Moreover, contrary to the other additive elements such as aluminum, it is less likely that Ag affects the heat conductivity of magnesium alloy adversely.

[0015] Note that, in the present description, the expressions such as "X-Y compounds" are compounds, in which "X" and "Y" make the major components, like those which are represented with such a compositional formula as "X_2Y," for instance.

[0016] Moreover, a magnesium-alloy cast product according to the present invention is a cast product that comprises the magnesium alloy for casting according to the present invention. The magnesium-alloy cast product according to the present invention is characterized in that it is obtainable by way of the following:

[0017] a molten-metal pouring step of pouring an alloy molten metal into a casting mold, the alloy molten metal including: copper (Cu) in an amount of from 1% by mass or more to 5% by mass or less; calcium (Ca) in an amount of from 0.1% by mass or more to 5% by mass or less; silver (Ag) in an amount of from 0.1% by mass or more to 5% by mass or less; and the balance comprising magnesium (Mg) and inevitable impurities; when the entirety is taken as 100% by mass; and

[0018] a solidifying step of solidifying the alloy molten metal after the molten-metal pouring step by cooling it.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] FIG. **1** is a graph for illustrating the heat conductivities of magnesium alloys whose alloy compositions differ.

[0020] FIG. **2** is a graph for illustrating the stress lowering magnitudes from the beginning of testing to 40 hours later in a stress relaxation test on magnesium alloys whose alloy compositions differ.

[0021] FIG. 3 is a graph in which compression stresses being applied to test specimens are plotted with respect to the testing time of the stress relaxation test for every 10 minutes.

[0022] FIG. 4A and FIG. 4B are photographs for substituting for drawings that show the metallic structure of Mg-3%-by-mass Cu-1%-by-mass Ca alloy (#01).

[0023] FIG. 5A and FIG. 5B are photographs for substituting for drawings that show the metallic structure of Mg-3%-by-mass Cu-1%-by-mass Ca-0.1%-by-mass Ag alloy (#02).

[0024] FIG. 6A and FIG. 6B are photographs for substituting for drawings that show the metallic structure of Mg-3%-by-mass Cu-1%-by-mass Ca-1%-by-mass Ag alloy (#03).

[0025] FIG. 7A and FIG. 7B are photographs for substituting for drawings that show the metallic structure of Mg-3%-by-mass Cu-1%-by-mass Ca-2%-by-mass Ag alloy (#04).

[0026] FIG. 8A and FIG. 8B are photographs for substituting for drawings that show the metallic structure of Mg-3%-by-mass Cu-1%-by-mass Ca-3%-by-mass Ag alloy (#05).

BEST MODE FOR CARRYING OUT THE INVENTION

[0027] Hereinafter, the best mode for carrying out the magnesium alloy for casting according to the present invention will be explained.

[0028] The magnesium alloy for casting according to the present invention is characterized in that it includes copper (Cu), calcium (Ca), silver (Ag), and the balance comprising magnesium (Mg) and inevitable impurities.

[0029] In the magnesium alloy for casting according to the present invention, the crystallized substances of Mg—Cu compounds and Mg—Ca compounds crystallize as network shapes (three-dimensionally mesh shapes) in crystalline grain boundaries between Mg crystalline grains by setting the contents of Cu, Ca and Ag to appropriate amounts. Since three-dimensionally mesh constructions with less discontinuous parts are formed in the crystalline grain boundaries, the effect of suppressing grain-boundary slip is high.

[0030] When the entire magnesium alloy for casting is taken as 100% by mass, the content of Cu is from 1% by mass or more to 5% by mass or less. When the content of Cu is 1% by mass or more, the Mg—Cu compounds crystallize sufficiently in the crystalline grain boundaries. When the content of Cu is less than 1% by mass, the strength is low because the crystallization of the Mg—Cu compounds to the crystalline grain boundaries is insufficient. A preferable content of Cu can be 2% by mass or more. Meanwhile, the greater the content of Cu is, the more excessive the amount of the Mg—Cu compounds that crystallize in the crystalline grain boundaries becomes, thereby turning into brittle structures so that the strength lowers. A preferable content of Cu can be 4% by mass or less.

[0031] The magnesium alloy for casting according to the present invention includes Ca and Ag along with Cu. It is believed that Ca and Ag exist in the crystalline grain boundaries along with Cu and thereby contribute to the formation of three-dimensionally mesh constructions. To be concrete, it is presumed that the Mg—Ca compounds crystallize in the crystalline grain boundaries along with the Mg—Cu compounds and then fine three-dimensionally mesh constructions are formed by means of the effect of the Ag addition.

[0032] When the entire magnesium alloy for casting is taken as 100% by mass, the content of Ca is from 0.1% by mass or more to 5% by mass or less. When the content of Ca is 0.1% by mass or more, the Mg—Ca compounds crystallize sufficiently in the crystalline grain boundaries. Moreover, since the ignition temperature of magnesium alloy rises when adding Ca to the magnesium alloy, the combustion that might occur when making the magnesium alloy into a molten metal is prevented. A preferable content of Ca can be 0.5% by mass or more. Meanwhile, when the content proportion of Ca surpasses 5% by mass, problems might arise in post-processing because the generation amount of the grain-boundary crystallized substances has become too much so that the mechanical strengths, such as the tensile strength and the elongation, lower. A preferable content of Ca can be 3% by mass or less, further preferably 2% by mass or less.

[0033] When the entire magnesium alloy for casting is taken as 100% by mass, the content of Ag is from 0.1% by mass or more to 5% by mass or less. When the content of Ag is 0.1% by mass or more, fine three-dimensionally mesh constructions are formed because the solid-liquid coexisting temperature range narrows down so that the Mg crystalline grains become micro-fine. The more the content proportion of Ag is the smaller the particle diameters of the Mg crystalline grains become; and additionally the widths of the grain-boundary crystallized substances thicken, and thereby the high-temperature strength and the creep resistance at high temperature improve; however, the more the content proportion of Ag is the more the flowability of the resulting molten metal tends to lower; and accordingly the cost goes up so that it is not economical. Consequently, the content of Ag is set to 5% by mass or less. A preferable content of Ag can be 4% by mass or less, further preferably 3% by mass or less.

[0034] Beginning with the fields of space, military and aviation, the magnesium alloy for casting according to the present invention being explained as above can be used in various fields, such as automobiles and electric instruments. Moreover, as a member comprising the magnesium alloy for casting according to the present invention, the following can be given, taking advantage of its characteristics at high temperature: products being utilized in high-temperature environments, for example, component parts constituting compressor, pumps and various cases that become high temperatures in service; moreover, engine component parts being used under high temperature and high load, especially, cylinder heads, cylinder blocks and oil pans of internal combustion engine, impellers for turbocharger of internal combustion engine, transmission cases being used for automobile and the like, and so forth.

[0035] Moreover, the magnesium-alloy cast product according to the present invention is a cast product that comprises the magnesium alloy for casting according to the present invention being detailed as above. Specifically, the magnesium-alloy cast product according to the present is a cast product that is obtainable by way of a molten-metal pouring step, and a solidifying step; the molten-metal pouring step is a step of pouring an alloy molten metal into a casting mold, the alloy molten metal including: copper (Cu) in an amount of from 1% by mass or more to 5% by mass or less; calcium (Ca) in an amount of from 0.1% by mass or more to 5% by mass or less; silver (Ag) in an amount of from 0.1% by mass or more to 5% by mass or less; and the balance comprising magnesium (Mg) and inevitable impurities; when the entirety is taken as 100% by mass; and the solidifying step is a step of solidifying the alloy molten metal after the molten-metal pouring step by cooling it.

[0036] The magnesium-alloy cast product according to the present invention is not limited to those made by ordinary gravity casting and pressure casting, but can even be those made by die-cast casting. Moreover, even the casting mold being utilized for the casting does not matter if it is sand molds, metallic molds, and the like. Since even the solidification rate (cooling rate) in the solidifying step is not limited in particular, it is allowable to properly select such an extent of solidification rate, which permits to form the three-dimensionally mesh constructions, depending on the size of ingots. Note that, when it is solidified at a usual solidification rate, the network-shaped metallic structure is obtainable.

[0037] Moreover, it is desirable that the magnesium alloy for casting and magnesium-alloy cast product according to the present invention can be an as-cast material. It is even allowable to improve the characteristics of the cast product by means of heat treating it after casting.

[0038] So far, the embodiment modes of the magnesium alloy for casting and magnesium-alloy cast product according to the present invention have been explained, however, the present invention is not one which is limited to the aforementioned embodiment modes. It can be conducted in various modes to which modifications, improvements, and the like, which one of ordinary skill in the art can carry out, are performed, within a range not departing from the scope of the present invention.

[0039] Hereinafter, while giving specific examples, the present invention will be explained in detail.

[0040] Test specimens whose contents of alloying elements in magnesium alloys were varied were made in a quantity of plural pieces, and then the evaluation of their characteristics and the observation of their metallic structures were carried out.

[0041] (Making of Test Specimens #01-#05)

[0042] A chloride-system flux was coated onto the inner surface of a crucible being made of iron that had been preheated within an electric furnace, and then a weighed pure magnesium base metal, pure Cu, and pure Ag, if needed, were charged into it and were then melted. Further, weighed Ca was added into this molten metal that was held at 750° C. (i.e., a molten-metal preparing step).

[0043] After fully stirring this molten metal to melt the raw materials completely, it was held calmly at the same temperature for a while. The thus obtained various alloy molten metals were poured into a metallic mold with a predetermined configuration (i.e., a molten-metal pouring step), and were then solidified in air atmosphere (i.e., a solidifying step), thereby casting test specimens (i.e., magnesium-alloy cast products) being labeled #01-#05. Note that the obtained test specimens had a size of 30 mm×30 mm×200 mm. The chemical compositions of the respective test specimens were specified in Table 1.

[0044] (Measurement of Heat Conductivity)

[0045] In addition to regarding the test specimens being labeled #01-#05 that were made with the aforementioned procedures, regarding similar test specimens that were made from the commercially available AZ91D (the composition is set forth in Table 1), the heat conductivities were found by means of laser flash method. The test results are specified in Table 1 and FIG. **1**.

[0046] (Stress Relaxation Test)

[0047] Onto test specimens being made from Test Specimens #01-#05 and AZ91D that are specified in Table 1, a stress relaxation test was carried out, thereby examining the creep resistances of the magnesium alloys. In the stress relaxation test, processes of how stresses decreased with time were measured, stresses which arose when a load was applied to the test specimens in the course of testing time until they exhibited a predetermined deformation magnitude. To be concrete, in 200° C. air atmosphere, a compression stress of 100 MPa was loaded to the test specimens, and then the compression stress was lowered in agreement with the elapse of time so as to keep the displacements of the test specimens at that time constant. The stress lowering magnitudes from the beginning of testing to 40 hours later are specified in Table 1 and FIG. **2**. Moreover, a graph is illustrated in FIG. **3**, graph which was prepared by plotting the compression stresses, which were applied to the test specimens, for every 10 minutes.

[0048] (Observation of Metallic Structure)

[0049] The surfaces of Test Specimens #01-#05 given in Table 1 were observed. The surface observation was carried out by observing cross sections, which were cut out of the respective test specimens, with a metallographic microscope. Although the metallic structures in the surfaces being labeled #01-#05 are shown in FIGS. **4**A-FIG. **8**A and in FIG. **4**B-**8**B, respectively, FIGS. **4**A-FIG. **8**A are for observing identical cross sections with (a) low magnification; and FIGS. **4**B-FIG. **8**B are for observing identical cross sections with (b) high magnification, in the respective drawings.

[0050] In Test Specimen #01, the three-dimensionally mesh constructions were confirmed, three-dimensionally mesh constructions which comprised intermetallic compounds that crystallized in crystalline grain boundaries, as can be appreciated from FIG. **4**A. Moreover, it was ascertained by means of EPMA (electron probe microanalyzer) and XRD (X-ray diffraction) that, in FIG. **4**B, those looking bright at the crystalline grain boundaries are $CuMg_2$ and those looking dark thereat are Mg_2Ca. Moreover, in Test Specimens #02-#05, the three-dimensionally mesh constructions were confirmed, three-dimensionally mesh constructions whose meshes were finer and continuities were higher than those of #01, as can be appreciated from FIGS. **5**A-FIG. **8**A. Moreover, it was ascertained by means of EPMA and XRD that, in FIG. **5**B-**8**B, those looking bright at the crystalline grain boundaries are $CuMg_2$ and those looking dark thereat are Mg_2Ca.

[0051] Note that, according to the EMPA and XRD, it was ascertainable that Ag exists mainly as Ag_3Mg at the crystalline grain boundaries in Test Specimens #02-#05.

TABLE 1

No.	Alloy Composition (% by mass)	Heat Conductivity (W/mK)	Stress Lowering Magnitude (MPa)
#01	Mg—3% Cu—1% Ca	155	65
#02	Mg—3% Cu—1% Ca—0.1% Ag	162	63
#03	Mg—3% Cu—1% Ca—1% Ag	154	59
#04	Mg—3% Cu—1% Ca—2% Ag	160	58
#05	Mg—3% Cu—1% Ca—3% Ag	156	56
AZ91D	Mg—9% Al—1% Zn	73	60

[0052] Any one of the test specimens being labeled #01-#05 were better than AZ91D in terms of the heat conductivity. Although the heat conductivity of the test specimens being labeled #01 that did not include any Ag was 155 W/mK, lowering of the heat conductivity that resulted from the addition of Ag was not seen in test specimens being labeled #02-#05.

[0053] Moreover, the greater the content of Ag was, the less the stress lowering magnitude was from the beginning of testing to 40 hours later in the stress relaxation test at 200° C. In particular, the respective test specimens being labeled #03, #04 and #05 exhibited better creep resistances over the period of from the beginning of testing to up to 40 hours than the test specimens being labeled #01, which did not include any Ag, and the test specimens being labeled AZ91D did (FIG. **3**).

[0054] Note that, in the aforementioned respective test specimens, the content of Cu was kept constant at 3% by mass and the content of Ca was kept constant at 1% by mass. Even in any one of the test specimens, they exhibit the heat conductivity and creep resistance to the same extent as those of the aforementioned respective test specimens when they fall in a range of from 2.7% by mass or more to 3.3% by mass or less for the case of being the content of Cu, and in a range of from 0.7% by mass or more to 1.3% by mass or less for the case of being the content of Ca.

[0055] Specifically, a magnesium alloy that includes Cu, Ca and Ag in the appropriate amounts does not show any lowering of the heat conductivity resulting from the addition of Ag, and is good in terms of the creep resistance at high temperature.

1. A magnesium alloy for casting, the magnesium alloy being characterized in that, when the entirety is taken as 100% by mass, it includes:

copper (Cu) in an amount of from 1% by mass or more to 5% by mass or less;

calcium (Ca) in an amount of from 0.1% by mass or more to 5% by mass or less;

silver (Ag) in an amount of from 0.1% by mass or more to 5% by mass or less; and

the balance comprising magnesium (Mg) and inevitable impurities.

2. The magnesium alloy for casting as set forth in claim **1**, wherein the content of said copper (Cu) is from 2% by mass or more to 4% by mass or less.

3. The magnesium alloy for casting as set forth in claim **1**, wherein the content of said calcium (Ca) is from 0.5% by mass or more to 3% by mass or less.

4. The magnesium alloy for casting as set forth in claim **1**, wherein the content of said silver (Ag) is from 0.1% by mass or more to 3% by mass or less.

5. The magnesium alloy for casting as set forth in claim **1** having a structure in which Mg—Cu compounds and Mg—Ca compounds are crystallized as network shapes in crystalline grain boundaries between Mg crystalline grains.

6. A magnesium-alloy cast product being characterized in that it is obtainable by way of the following:

a molten-metal pouring step of pouring an alloy molten metal into a casting mold, the alloy molten metal including: copper (Cu) in an amount of from 1% by mass or more to 5% by mass or less; calcium (Ca) in an amount of from 0.1% by mass or more to 5% by mass or less; silver (Ag) in an amount of from 0.1% by mass or more to 5% by mass or less; and the balance comprising magnesium (Mg) and inevitable impurities; when the entirety is taken as 100% by mass; and

a solidifying step of solidifying the alloy molten metal after the molten-metal pouring step by cooling it.

7. The magnesium-alloy cast product as set forth in claim **6** having a structure in which Mg—Cu compounds and Mg—Ca compounds are crystallized as network shapes in crystalline grain boundaries between Mg crystalline grains.

* * * * *