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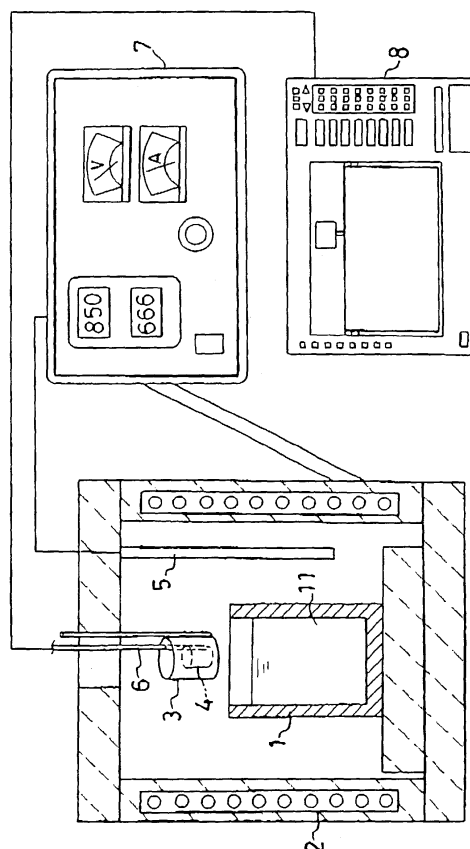
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(54) **Method for grain refinement of magnesium alloy castings**

(57) A method for grain refinement of magnesium alloy castings includes adding graphite (C) powder and manganese dioxide (MnO_2) to a melt of magnesium alloy containing aluminum (Al) and manganese (Mn) to finely divide crystal grains of a cast structure.

FIG. 1



Description

[0001] This invention relates to a method for grain refinement of magnesium alloy castings, which method is capable of grain refinement of solidified structure of the cast product and improving the mechanical properties thereof without generating dioxin.

Description of the Prior Art:

[0002] The method for the grain refinement of aluminum (Al)-containing magnesium alloy, such as the AZ type, is known in two kinds, namely a method that shuns addition of a grain refiner and a method that necessitates addition of the grain refiner.

[0003] The former method includes a method of superheat-treatment that comprises superheating the whole of molten alloy to about 850°C to 900°C (1123K to 1173K), holding it for about 5 minutes to 15 minutes (0.3 ks to 0.9 ks), cooling it at a rate of 150°C/min or more, and thereafter quenching it at the casting temperature. The mechanism of grain refinement of the superheat-treatment is considered to nucleate an Al-Mn-(Fe) compound. Since this method of superheat-treatment requires an inevitably high treating temperature, however, it incurs undue cost of energy, boosts the expense for preventing the molten alloy from oxidation and performing works of maintenance and inspection on the crucible, and entails the problem of imperiling economy and safety.

[0004] The latter method includes carbon addition that comprises adding a carbon (C)-containing compound at a temperature in the neighborhood of 750°C to the molten alloy. The mechanism of grain refinement by carbon addition is considered to nucleate aluminum carbide (Al_4C_3) resulting from the reaction of carbon in a compound with aluminum in the molten alloy. Commercially, the practice of adding hexachloroethane (C_2Cl_6) as the grain refiner has prevailed. Since the hexachloroethane induces generation of dioxins {2,3,7,8-tetrachloro-dibenzo-p-dioxin: $\text{Cl}_2(\text{C}_6\text{H}_2)\text{O}_2(\text{C}_6\text{H}_2)\text{Cl}_2$ }, the use thereof is now prohibited.

[0005] The latter method further includes a method of Carbon Addition by Blowing that comprises directly blowing a graphite (C) powder together with argon gas (Ar) into the molten alloy (refer, for example, to JP-A 2003-41331). This method of Carbon Addition by Blowing is capable of grain refinement of the solidified structure without inducing generation of dioxins.

[0006] The carbon that is added by blowing, however, can promote the grain refinement of the solidified structure proportionately to the rise of the temperature of the molten alloy. Though the method of Carbon Addition by Blowing indeed defies generation of dioxins, it requires heightening the temperature of treatment for the purpose of promoting the grain refinement of the solidified structure and entails the problem of incurring the cost of energy. This invention aims to provide a method for fine grain refinement of magnesium alloy castings while encouraging decrease of the cost of energy, promoting the grain refinement of the solidified structure and improving the mechanical properties of the magnesium alloy castings without inducing generation of dioxins.

[0007] For the sake of accomplishing the object described above, the method contemplated by this invention for fine grain refinement of the magnesium alloy castings comprises adding a graphite (C) powder and manganese dioxide (MnO_2) into a melt of magnesium alloy containing aluminum (Al) and manganese (Mn), thereby enabling crystal grains of a cast structure to be refined finely.

[0008] In the method for fine grain refinement of the magnesium alloy castings, the addition of a graphite (C) powder and manganese dioxide (MnO_2) embraces the case of them being added as contained in a metallic capsule formed of pure aluminum, aluminum alloys, pure magnesium or magnesium alloys.

[0009] The amount of the manganese dioxide (MnO_2) to be added is in the range of 0.10 mass% to 0.22 mass%, preferably in the range of 0.20 mass% to 0.22 mass%, based on the mass of the molten magnesium alloy mentioned above.

[0010] According to this invention, since a graphite powder and manganese dioxide are added to the molten magnesium alloy, the temperature of the molten alloy can be elevated by the reaction of oxidation-reduction with the manganese dioxide. Since both the addition of hexachloroethane and the generation of dioxins are absent, the cost of energy can be decreased, the grain refinement of a crystal can be promoted, and the mechanical properties of the cast article of magnesium alloy can be improved. Then, since the graphite powder and the manganese dioxide are allowed to be contained in a metallic capsule, the graphite powder and the manganese dioxide can be prevented from being scattered and can be utilized efficiently in small amounts for the grain refinement. Further, since the metallic capsule is made of aluminum alloy or magnesium alloy, they can participate in effecting the grain refinement without adversely affecting the components of the composition of the alloy. Since manganese dioxide is added in an amount in the range of 0.10 mass% to 0.22 mass% based on the mass of the molten magnesium alloys, it enables the crystal grains to be finely divided to an average particle diameter of 170 μm or less. Since manganese dioxide is added in an amount in the range of 0.20 mass% to 0.22 mass% based on the mass of the molten magnesium alloys, it enables the grain refinement to be effected to the same degree as the addition of hexachloroethane.

[0011] The invention will become more apparent to those skilled in the art from the description to be made herein below with reference to the accompanying drawings, in which:

[0012] Fig. 1 shows a schematic illustration of an apparatus used in the method for fine grain refinement according to this invention,

[0013] Fig. 2 shows a process diagram illustrating a procedure of this invention, starting with melting alloy and finishing with casting the molten alloy in a metallic mold,

[0014] Fig. 3 is a diagram illustrating changes of the temperature in a phosphorizer and the temperature of the melt caused by the addition of manganese dioxide,

[0015] Fig. 4 is a copy of optical microphotographs showing the solidified structure of an untreated material and the solidified structure of a manganese dioxide-added treated material resulting from adding manganese dioxide in an amount of 0.20 mass% based on the mass of molten alloy,

[0016] Fig. 5 shows a copy of optical microphotographs showing the solidified structure of a hexachloroethane-added treated material, that of an untreated material and that of a capsule-added treated material, respectively,

[0017] Fig. 6 shows a copy of optical microphotographs showing the solidified structures of graphite-added treated materials having the amount of added graphite sequentially increased,

[0018] Fig. 7 shows a characteristic diagram showing the relation between the amount of graphite added and the average particle diameter of crystal grains,

[0019] Fig. 8 shows a copy of optical microphotographs showing the solidified structures of various complex-added treated materials having the amount of added graphite varied,

[0020] Fig. 9 shows a characteristic diagram showing the relation between various complex-added materials and the average particle diameters of crystal grains,

[0021] Fig. 10 shows a copy of optical microphotographs showing the solidified structures of various complex-added treated materials having the amount of added MnO_2 varied,

[0022] Fig. 11 shows a characteristic diagram showing the relation between various complex-added materials and average particle diameters of crystal grains,

[0023] Fig. 12 shows a copy of an optical microphotograph showing the solidified structure of a complex-added treated material using a graphite powder having a diameter on the order of nm,

[0024] Fig. 13 shows a characteristic diagram showing tensile strength, 0.2% proof strength (MPa) and elongation (%) in the F specimen of an untreated material, a manganese dioxide-added treated material, a hexachloroethane-added treated material and a complex-added treated material, and

[0025] Fig. 14 shows a characteristic diagram showing tensile strength, 0.2% proof strength (MPa) and elongation (%) in the T4 specimen of an untreated material, a manganese dioxide-added treated material, a hexachloroethane-added treated material and a complex-added treated material.

[0026] The method according to this invention for fine grain refinement of the magnesium alloy castings comprises adding a graphite (C) powder and manganese dioxide (MnO_2) to a melt of magnesium alloy containing aluminum (Al) and manganese (Mn) to enable crystals of a cast structure to be finely refined. The magnesium alloy containing aluminum and manganese does not need to be particularly restricted with respect to its composition. The AZ91E alloy that contains aluminum in the composition and manganese as an impurity is used also for sand casting as will be described specifically herein below may be used as such magnesium alloy.

[0027] The graphite powder to be used in this invention does not need to be particularly restricted to the graphite 5 μm in particle diameter mentioned in an example cited herein below. Commendably, it has the smallest possible diameter. Good results are obtained by using a graphite powder having a diameter of the order of nanometer (nm), for example.

[0028] The manganese dioxide to be used in this invention is depicted as a powder 100 μm in particle diameter in an example to be cited herein below, it may be formed massively (such as in the shape of tablets and pellets). The amount (mass%) of the manganese dioxide to be added falls preferably in the range of 0.10 mass% to 0.22 mass% and more preferably in the range of 0.20 mass% to 0.22 mass% based on the amount (mass) of the melt of magnesium alloy. If the amount of manganese dioxide added falls short of 0.10 mass%, the shortage will result in preventing the effect of grain refinement from being manifested fully satisfactorily. If the amount of manganese dioxide added exceeds 0.22 mass%, the excess will not bring a proportionate addition to the effect of grain refinement. Incidentally, the particle diameter level of the magnesium alloy castings in an untreated state is about 30 μm . The effect of grain refinement becomes discernible when the particle diameter falls short of this level. Since the solidified structure of alloy is preferred to possess the finest possible particle diameter, the conditions for obtaining as high an effect of grain refinement as possible are aimed at a particle diameter which equals the particle diameter attained by the method resorting to the addition of hexachloroethane.

[0029] In this invention, it is commendable to add a graphite powder and manganese dioxide as contained in a metallic capsule. By having the graphite powder and manganese dioxide contained in a metallic capsule, it is made possible to prevent the graphite powder and manganese dioxide from being scattered and utilize them efficiently in

small amounts for the grain refinement. Further, since the metallic capsule is made of pure aluminum or aluminum alloy or of pure magnesium or magnesium alloy, they are enabled to effect the grain refinement without adversely affecting the composition of the alloy.

[0030] Fig. 1 shows a schematic view illustration of the apparatus that is used in the examples of this invention. Referring to Fig. 1, reference numeral 1 denotes a crucible that is formed of iron (Fe)-chromium (Cr)-based SUS 430 stainless steel (Fe-18% Cr) containing no nickel (Ni) and is manufactured by bending this stainless steel plate in a cylindrical shape and gas welding the seam. Further, for the purpose of enhancing the ability to resist high-temperature oxidation, the crucible is subjected to immersion plating in a pure aluminum bath and the layer of pure aluminum formed thereon is subjected to thermal diffusion so as to coat the surface of the crucible 1 with a FeAl_3 layer sparingly liable to be wetted by magnesium. All the casting implements including the crucible 1 are coated with magnesium oxide of the reagent chemical grade so as to prevent inclusion of impurities during the melting of alloy.

[0031] Denoted by reference numeral 2 is an electric furnace and by numeral 3 is a phosphorizer. The phosphorizer 3 which is destined to be passed through a hole in the lid of the electric furnace 2 and immersed in molten alloy 11 held in the crucible 1 is made to hold therein a metallic capsule 4 accommodating a graphite (C) powder or manganese dioxide (MnO_2), or accommodating a graphite powder and manganese dioxide. Incidentally, the phosphorizer 3 is manufactured in the same manner as the crucible 1. The metallic capsule is formed of pure aluminum or aluminum alloy, or pure magnesium or magnesium alloy. As the graphite powder, graphite (purity of 99.9% and particle size of about 5 μm) made by Kojundo Kagaku Kenkyusho Ltd. and sold under the product designation of "Pure Carbon." was used. As the manganese dioxide, a reagent chemical grade manganese dioxide (purity of 99.9% and particle size of about 100 μm) made by Takaraitesuku K.K. was used.

[0032] Denoted by reference numerals 5 and 6 are thermocouples. The thermocouple 5 is set inside the electric furnace 2 for the purpose of measuring the temperature of the interior of the electric furnace 2, and the thermocouple 6 is set in the phosphorizer 3 next to the metallic capsule 4 to measure the temperature of the molten alloy 11. A temperature-controlling device is labeled with 7. It is intended to control the temperature of the interior of the electric furnace 2, namely the temperature of the molten alloy 11 at a prescribed temperature, based on the output of the thermocouple 5. A pen recorder is labeled with 8. It serves to record the temperature of the molten alloy 11 based on the output of the thermocouple 6.

[0033] Now, the method for testing the effect of the addition of manganese dioxide on the grain refinement of crystals will be described below.

[0034] For the test, commercially available AZ91E magnesium alloy having a composition shown in Table 1 below was used. The test was performed through the procedure shown in Fig. 2. The amounts, in mass%, of graphite powder and/or manganese dioxide added in the individual runs of this test were as shown in Table 2 below.

Table 1

Al	Zn	Mn	Si	Cu	Ni	Fe	Mg
9.01	0.82	0.22	0.01	0.001	0.002	0.0017	Balance

Table 2

Graphite-added treated material	Complex-added treated material	Variation in amount of MnO_2 added
Amount of graphite powder added (mass%)	Amount of graphite powder added (%), with added amount of MnO_2 fixed at 0.20 mass%	Amount of MnO_2 added (%), with added amount of graphite powder fixed at 0.02 mass%
0.005	0.04	0.30
0.01	0.02	0.20
0.02	0.01	0.10
0.04	0.005	0
0.06	0.003	-
0.08	0.001	-

[0035] First, the question whether or not the addition of manganese dioxide induces a rise of temperature was studied. For a start, 700 g of AZ91E magnesium alloy pickled with nitric acid for the purpose of depriving the surface thereof of impurities was melted in the electric furnace 2, and the resultant molten alloy 11 was heated to 800°C. Then, the

metallic capsule 4 accommodating therein manganese dioxide in an amount of 0.20 mass% based on the mass of the molten alloy 11 was set in place in the phosphorizer 3, and the phosphorizer 3 was inserted together with the thermocouple 6 into the molten alloy 11. Manganese dioxide was added to the molten alloy 11 while the measurement of temperature was continued meantime. Then, the molten alloy 11 was left cooling outside the electric furnace 2 to 700°C and cast in a metallic mold held at room temperature. An untreated sample was also made without adding manganese dioxide, with the object of investigating the effect of addition of manganese dioxide on a solidified structure.

[0036] The amount of manganese dioxide to be added was decided, with due respect to the fact that the manganese content in the AZ91E magnesium alloy conforming to the ASTM standard shown in Table 3 below is in the range of 0.17 mass% to 0.35 mass%, at the maximum such that the total amount of the manganese content in the commercially available AZ91E magnesium alloy and the amount of manganese separated as reduced in the molten alloy 11 in consequence of the addition of manganese dioxide may not surpass the upper limit of the range of the manganese content in the AZ91E magnesium alloy conforming to the ASTM standard. The reason for using this maximum is that the actual manganese content conforms the ASTM standard and shuns exertion of adverse effect on the components of the composition of the alloy.

Table 3

Al	Zn	Mn	Si	Cu	Ni	Fe	Impurity	Mg
8.1~9.3	0.40~1.0	0.17~0.35	0.20	0.015	0.0010	0.005	0.01	Balance

[0037] When manganese dioxide was added as described above, it induced an oxidation-reduction reaction and consequently varied the temperature of the interior of the phosphorizer 3 and the temperature of the whole of the molten alloy 11, as shown in Fig. 3. It is clear from Fig. 3 that the interior of the phosphorizer 3 showed a discernible sign of temperature elevation, though instantaneously, to the neighborhood of about 1370°C (1643 K). The temperature of the whole of the molten alloy 11, however, showed virtually no discernible change. The oxidation-reduction reaction that was caused by the addition of manganese dioxide, therefore, was found to be a reaction that elevated the temperature inside the phosphorizer 3 or in a narrow region encompassing the phosphorizer 3.

[0038] The solidified structure, magnified by an optical microscope, of an untreated material of the molten alloy 11 having nothing added thereto and the solidified structure, magnified by an optical microscope, of a manganese dioxide-added treated material having manganese dioxide added in an amount of 0.20 mass% based on the mass of the molten alloy 11 are shown in Fig. 4. From Fig. 4, it may be safely inferred that manganese dioxide has no effect of grain refinement of the solidified structure.

[0039] Now, the effect manifested by the sole addition of a graphite powder on the grain refinement of the solidified structure was studied. First, 700 g of AZ91E magnesium alloy pickled with nitric acid for the purpose of depriving the surface thereof of impurities was melted in the electric furnace 2, and the temperature of the molten alloy 11 was elevated to 800°C by following the procedure shown in Fig. 2. Then, the graphite powder of a gradually increased amount, namely 0.005 mass%, 0.01 mass%, 0.02 mass%, 0.04 mass%, 0.06 mass% and 0.08 mass% each, based on the mass of the molten alloy 11 as shown in Table 2 was added as held in the metallic capsule 4 to the interior of the phosphorizer 3. The sample which had the graphite powder added thereto and had undergone the treatment will be referred to as "graphite-added treated material." For the purpose of comparing and studying the degree of grain refinement of a solidified structure caused by the addition of graphite, a sample having hexachloroethane (C₂Cl₆) added thereto (conditions of addition: temperature of addition of 750°C, amount of addition: 1 mass% based on the mass of the molten alloy 11) (hexachloroethane-added treated material) was also manufactured. Then, for the purpose of studying the effect of the metallic capsule 4 formed of magnesium alloy on the solidified structure, a sample having the metallic capsule 4 alone added thereto (a capsule-added treated material) was manufactured. The metallic capsule 4 was a product obtained by preparing a blind container measuring 19 mm in outside diameter 15 mm in inside diameter, 20 mm in height and 2 mm in wall thickness and sealing the container with a lid 2 mm in wall thickness.

[0040] The solidified structure, magnified by an optical microscope, of the hexachloroethane-added treated material, the solidified structure, magnified by an optical microscope, of the untreated material and the solidified structure, magnified by an optical microscope, of the capsule-added treated material are shown in Fig. 5. The solidified structure, magnified by an optical microscope, of the graphite-added treated material having the graphite powder content gradually increased as described above is shown in Fig. 6. The relation (characteristic) between the amount of the graphite powder added and the average crystal grain diameter is shown in Fig. 7. For the purpose of allowing visual observation of the structure, the sample obtained by performing a solution treatment under the conditions of 673 K and 14.4 ks with the object of transforming a eutectic crystal generated by quenching into a solid solution was tested for average crystal grain diameter by the slice method using an optical microscope. The average crystal grain diameters reported hereinafter were determined in the same manner.

[0041] From Fig. 5 which shows that the untreated material and the capsule-added treated material formed equal

solidified structures, it may be safely inferred that the metallic capsule 4 had no effect of fine grain refinement. Hexachloroethane, however, had an effect of fine grain refinement as clearly noted from Fig. 5. It is clearly noted from Fig. 6 and Fig. 7 that the treated materials having the graphite powder added in the amounts of 0.005 mass%, 0.01 mass% and 0.02 mass% each had an average crystal grain diameter of 300 μm equal to that of the untreated materials. From the data, it may be safely inferred that the graphite powder had no effect of grain refinement. When the amount of the graphite powder added reached 0.04 mass%, the average crystal grain particle became 180 μm . Thus, the effect of grain refinement was attained to a certain extent. When the amount of the graphite powder added further rose to 0.06 mass% and 0.08 mass%, the average crystal grain diameter became substantially constant at about 70 μm . Thus, the effect of grain refinement in this case equaled that obtained by the addition of hexachloroethane. The smallest amount of the graphite powder required to be added for the sake of grain refinement of the solidified structure, therefore, is 0.04 mass%. For the purpose of obtaining the same effect of grain refinement as the hexachloroethane-added treated material, the amount of addition is required to exceed 0.06 mass%.

[0042] Next, the effect brought by the addition of a graphite powder and manganese dioxide on the grain refinement of the solidified structure was investigated. First, 700 g of AZ91E magnesium alloy pickled with nitric acid for the purpose of depriving the surface thereof of impurities was melted by the electric furnace 2 and the temperature of the molten alloy 11 was elevated to 800°C by following the procedure shown in Fig. 2. Then, the manganese dioxide in a fixed amount of 0.20 mass% and the graphite powder of a gradually decreased amount, namely 0.04 mass%, 0.02 mass%, 0.01 mass%, 0.005 mass%, 0.003 mass% and 0.001 mass% each, based on the mass of the molten alloy 11 as shown in Table 2 were added as held in the metallic capsule 4 to the interior of the phosphorizer 3. The material resulting from the addition of a complex additive, namely graphite powder plus manganese dioxide, and the subsequent treatment will be referred to as a "complex-added treated material."

[0043] The solidified structures, magnified by an optical microscope, of various complex-added treated materials mentioned above are shown in Fig. 8 and the relation (characteristic) between the various complex additives and the average crystal grain diameters is shown in Fig. 9. It is clearly noted from Fig. 8 and Fig. 9 that the amounts of the graphite powder added were 0.04 mass% and 0.02 mass%, the average crystal grain diameters became substantially constant at about 70 μm . Thus, the effect of grain refinement of the solidified structure obtained here was equal to that obtained by the addition of hexachloroethane. When the amount of the graphite powder added was 0.01 mass% or less, however, the trend of the crystal grains toward coarsening proportionately to the decrease of the amount of addition of the graphite powder became visible. A discussion based on Fig. 6 to Fig. 9, therefore, leads to an inference that in the case of the addition of the graphite powder in a fixed amount, the complex-added treated material had a higher effect of grain refinement of the solidified structure than the treated material which had no graphite powder added thereto and that the complex-added treated material having the graphite powder added in an amount of 0.02 mass% or more obtained the same effect of grain refinement of the solidified structure as the addition of hexachloroethane. This phenomenon may be logically explained by a supposition that in consequence of the addition of both manganese dioxide and the graphite powder, the oxidation-reduction reaction occurred locally at the position adjoining graphite and the elevation of temperature due to the generation of heat by the reaction promoted the formation of Al_4C_3 , a nucleus-forming substance. Though the optimum amount of addition of graphite in the complex-added treated material is 0.02 mass%, it is commendable for the purpose of securing the effect of grain refinement of the solidified structure to fix the amount of addition of graphite at 0.01 mass% or more and 0.1 mass% or less.

[0044] Next, the effect brought by the change in the amount of addition of manganese dioxide on the refinement of crystal grains was investigated. First, 700 g of AZ91E magnesium alloy pickled with nitric acid for the purpose of depriving the surface thereof of impurities was melted by the electric furnace 2 and the temperature of the molten alloy 11 was elevated to 800°C by following the procedure shown in Fig. 2. Then, the graphite powder in a fixed amount of 0.20 mass% and the manganese dioxide of a gradually decreased amount, namely 0.30 mass%, 0.20 mass%, 0.10 mass% and 0 mass% each, based on the mass of the molten alloy 11 as shown in Table 2 were added as held in the metallic capsule 4 to the interior of the phosphorizer 3.

[0045] The solidified structures, magnified by an optical microscope, of the various complex-added treated materials are shown in Fig. 10, and the relation (characteristic) between the various complex additives and the average crystal grain diameters, is shown in Fig. 11. It is clearly noted from Fig. 10 and Fig. 11 that when manganese dioxide was added in amounts of 0.30 mass% and 0.20 mass%, the average crystal grain diameters became substantially constant at about 70 μm . Thus, the effect of grain refinement of the solidified structure obtained here equaled that obtained by the addition of hexachloroethane. When the amount of addition of manganese dioxide fell short of 0.10 mass%, however, the trend of crystal grains toward coarsening proportionately to the decrease of the amount of addition of manganese dioxide became visible. In the complex-added treated material having the graphite powder added in a fixed amount, therefore, it is inferred in view of the data of Fig. 11 that the addition of manganese dioxide in an amount of 0.10 mass% or more resulted in bringing the effect of grain refinement having an average crystal grain diameter of about 170 μm or less and the addition of manganese dioxide in an amount of 0.20 mass% or more resulted in bringing the same effect of refined crystal grains as in the case of adding hexachloroethane. Though the optimum amount of

addition of manganese dioxide in the complex-added treated material is 0.2 mass%, it is commendable for the purpose of securing the effect of grain refinement of the solidified structure to fix the amount of addition of manganese dioxide at 0.10 mass% or more and 0.4 mass% or less.

[0046] Next, the effect brought by the particle diameter of graphite powder on the grain refinement of the solidified structure was investigated. First, 700 g of an AZ91E magnesium alloy pickled with nitric acid for the purpose of depriving the surface thereof of impurities was melted by the electric furnace 2 and the temperature of the molten alloy 11 was elevated to 800°C by following the procedure shown in Fig. 2. Then, carbon nanotubes in an amount of the nm order of 0.2 mass%, such as 100 nm in diameter and 5 μm in length, based on the mass of the molten alloy 11 and manganese dioxide in an amount of 0.20 mass% based on the mass of the molten alloy 11 were added as held in the metallic capsule 4 into the phosphorizer 3.

[0047] The solidified structure, magnified by an optical microscope, of the complex-added treated material mentioned above is shown in Fig. 12. It is clearly noted from Fig. 12 that the average crystal grain diameters became substantially constant at about 75 μm and the effect of grain refinement of the solidified structure obtained here equaled that obtained by the addition of hexachloroethane. Thus, the graphite obtained the effect of grain refinement of the solidified structure equaling that obtained by the addition of hexachloroethane even when the particle diameter of the graphite was changed to the nm order.

[0048] Next, the F specimens (specimens as cast) and the T4 specimens (specimens having undergone a treatment for transformation into a solid solution, specifically heat-treated at 400°C for 16 hours) of the various treated materials were tested for tensile strength, 0.2% proof strength (MPa) and elongation (%). First, Fig. 13 is a characteristic diagram showing the data of tensile strength, 0.2% proof strength (MPa) and elongation (%) obtained of the F specimens of the untreated material, manganese dioxide-added treated material, hexachloroethane-added treated material and complex-added treated material. Then, Fig. 14 is a characteristic diagram showing the data of tensile strength, 0.2% proof strength (MPa) and elongation (%) obtained of the T4 specimens of the untreated material, manganese dioxide-added treated material, hexachloroethane-added treated material and complex-added treated material.

[0049] It is clearly noted from Fig. 13 and Fig. 14 that the F specimens and the T4 specimens of the complex-added treated materials equaled the F specimens and the T4 specimens of the hexachloroethane-added treated material in terms of tensile strength, 0.2% proof strength and elongation.

[0050] The preceding example depicted a case of using an AZ91E magnesium alloy as a magnesium alloy. The castings shown in Table 4 below, for example, may be used instead so long as they are magnesium alloys containing aluminum (Al) and manganese (Mn). As the graphite powder, a carbon nanotube measuring 100 nm in diameter and 5 μm in length has been cited above. Carbon nanotubes measuring 50 nm to 200 nm in diameter and 1 μm to 20 μm in length are capable of producing similar effects.

Table 4

Kind of article of cast metal	Chemical compositions (mass%)								
	Al	Zn	Mn	Si	Cu	Ni	Fe	Impurity	Mg
1 st grade	5.36~6.7	2.5~3.5	0.15~0.35	≤D.30	≤0.25	≤0.01	-	≤0.30	Balance
2 nd grade C	8.1~9.3	0.40~1.0	0.13~0.35	≤0.30	≤0.10	≤0.01	-	≤0.30	Balance
2 nd grade E	8.1~9.3	0.40~1.0	0.17~0.35	≤0.20	≤0.015	≤0.0010	≤0.005	≤0.30	Balance
3 rd grade	8.0~10.0	1.5~2.5	0.10~0.5	≤0.3	≤0.20	≤0.01	≤0.05	≤0.30	Balance
5 th grade	9.3~10.7	≤0.3	0.10~0.35	≤0.30	≤0.10	≤0.01	-	≤0.30	Balance
ISO 1 st grade	5.00~7.0	2.0~3.5	0.10~0.5	≤0.3	≤0.2	≤0.01	≤0.05	-	Balance
ISO 2 nd grade A	7.0~9.5	0.3~2.0	≤0.15	≤0.5	≤0.35	≤0.02	≤0.05	-	Balance
ISO 2 nd grade B	7.50~9.0	0.2~1.0	0.15~0.6	≤0.3	≤0.2	≤0.01	≤0.05	-	Balance
ISO 3 rd grade	8.3~10.3	0.2~1.0	0.15~0.6	≤0.3	≤0.2	≤0.01	≤0.05	-	Balance

[0051] According to this invention, owing to the addition of manganese dioxide besides a graphite powder to the melt of magnesium alloy, it is made possible to utilize the reaction of oxidation-reduction caused by manganese dioxide for elevating the temperature of the molten alloy, promoting the grain refinement of the solidified structure by carbon, and materializing production of a cast article of the magnesium alloy which enjoys improved mechanical properties. This invention is enabled by the avoidance of addition of hexachloroethane to shun the generation of dioxins and by the utilization of the reaction of oxidation-reduction of manganese dioxide to elevate the temperature of the melt of magnesium alloy and promote the decrease of the cost of energy consequently and enjoy the same effect as in the case of adding hexachloroethane.

Claims

1. A method for grain refinement of magnesium alloy casting, comprising adding graphite (C) powder and manganese dioxide (MnO_2) to a melt of magnesium alloy containing aluminum (Al) and manganese (Mn) to refine crystal grains of a cast structure.
2. The method according to claim 1, wherein said graphite (C) powder and said manganese dioxide (MnO_2) are accommodated in a metallic capsule.
3. The method according to claim 2, wherein said metallic capsule is formed of pure aluminum, aluminum alloy, pure magnesium or magnesium alloy.
4. The method according to claim 2, wherein said metallic capsule is formed of pure magnesium or magnesium alloy.
5. The method according to any one of claims 1 to 4, wherein said manganese dioxide (MnO_2) has an amount in the range of 0.10 mass% to 0.22 mass% based on a mass of the melt of said magnesium alloy.
6. The method according to any one of claims 1 to 4, wherein said manganese dioxide (MnO_2) has an amount in the range of 0.20 mass% to 0.22 mass% based on a mass of the melt of said magnesium alloy.

FIG. 1

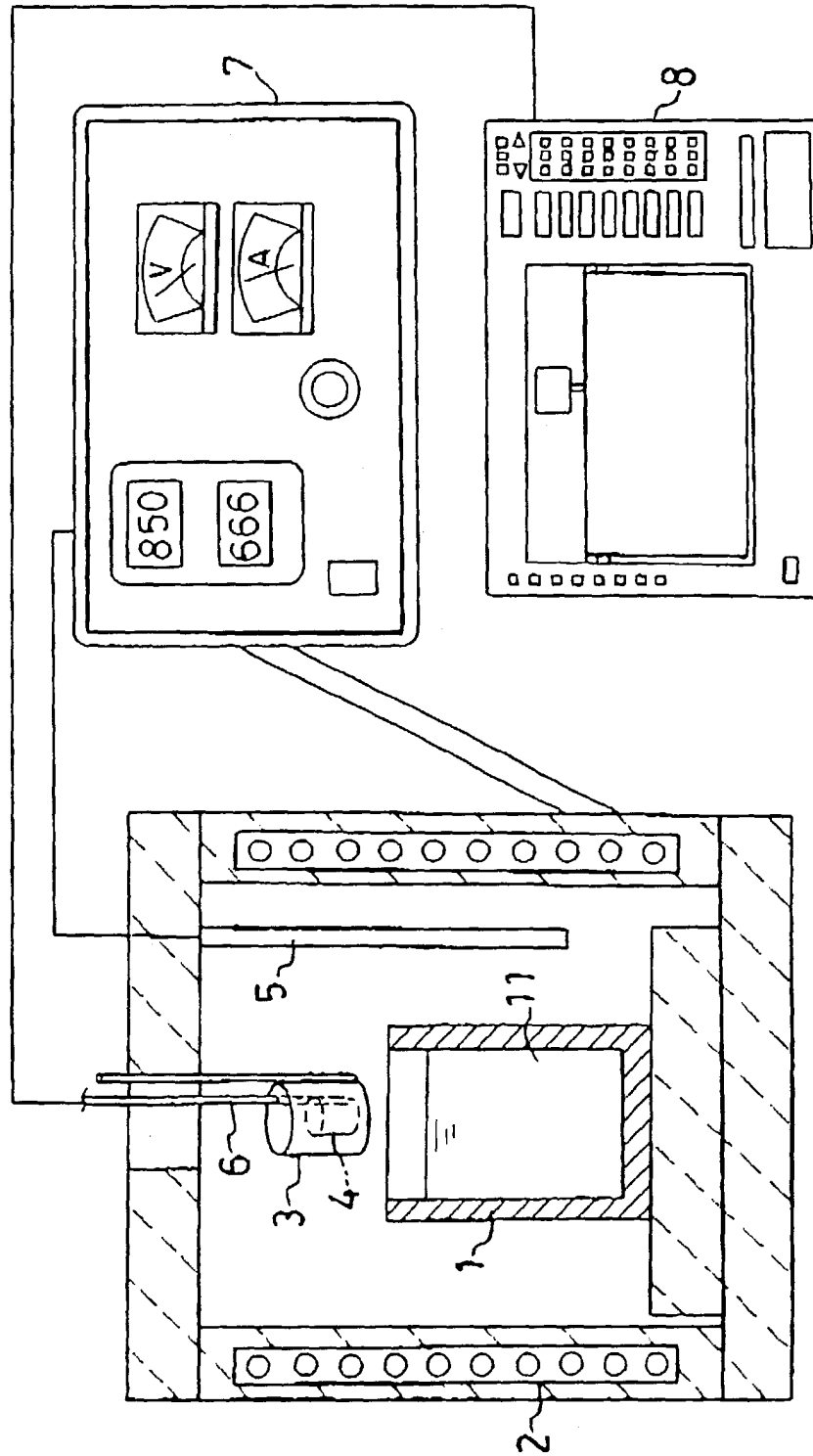


FIG. 2

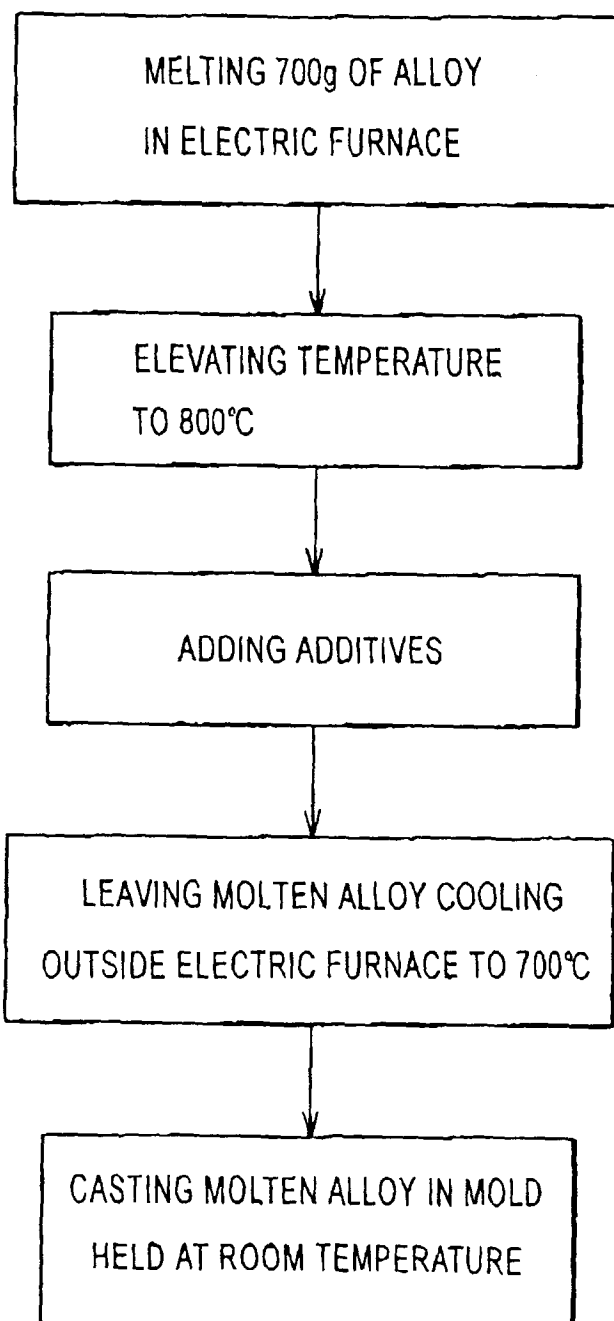


FIG. 3

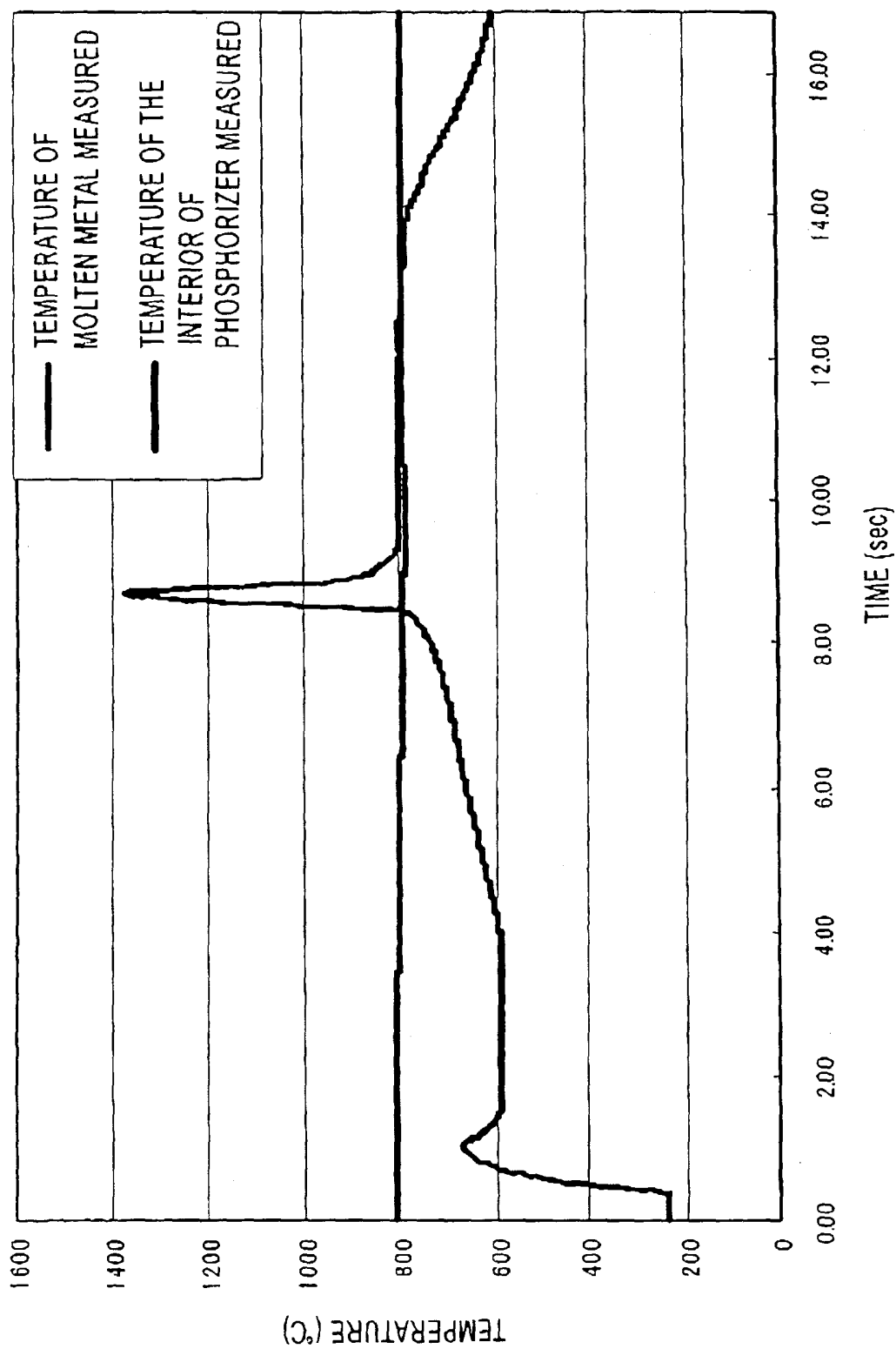


FIG. 4

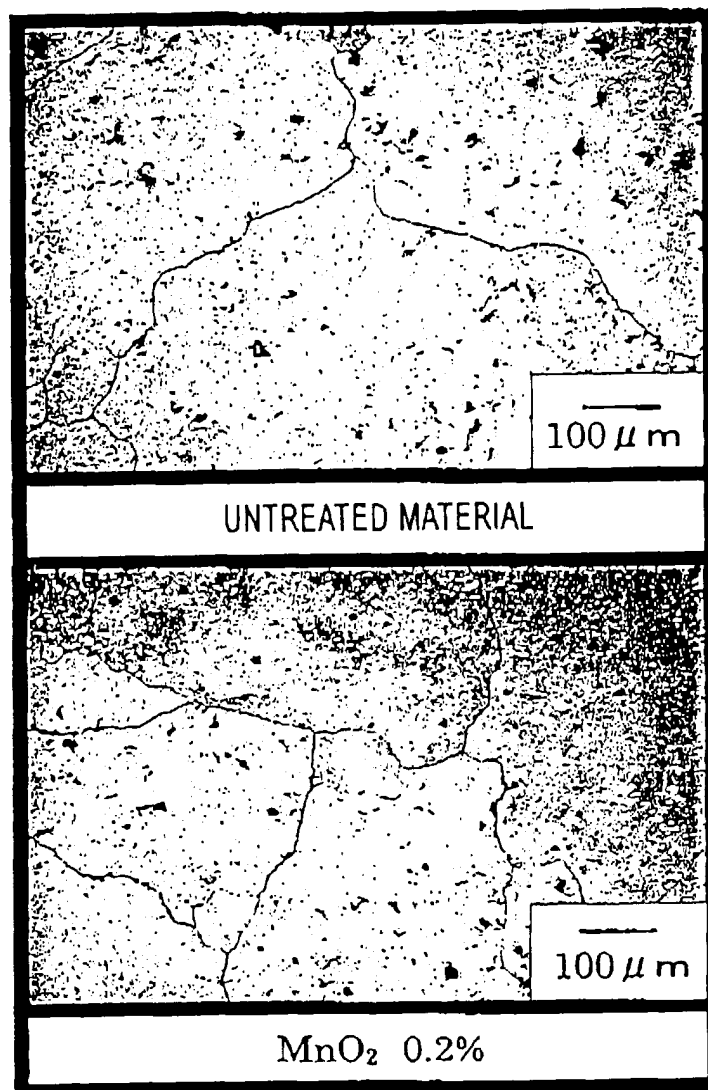


FIG. 5

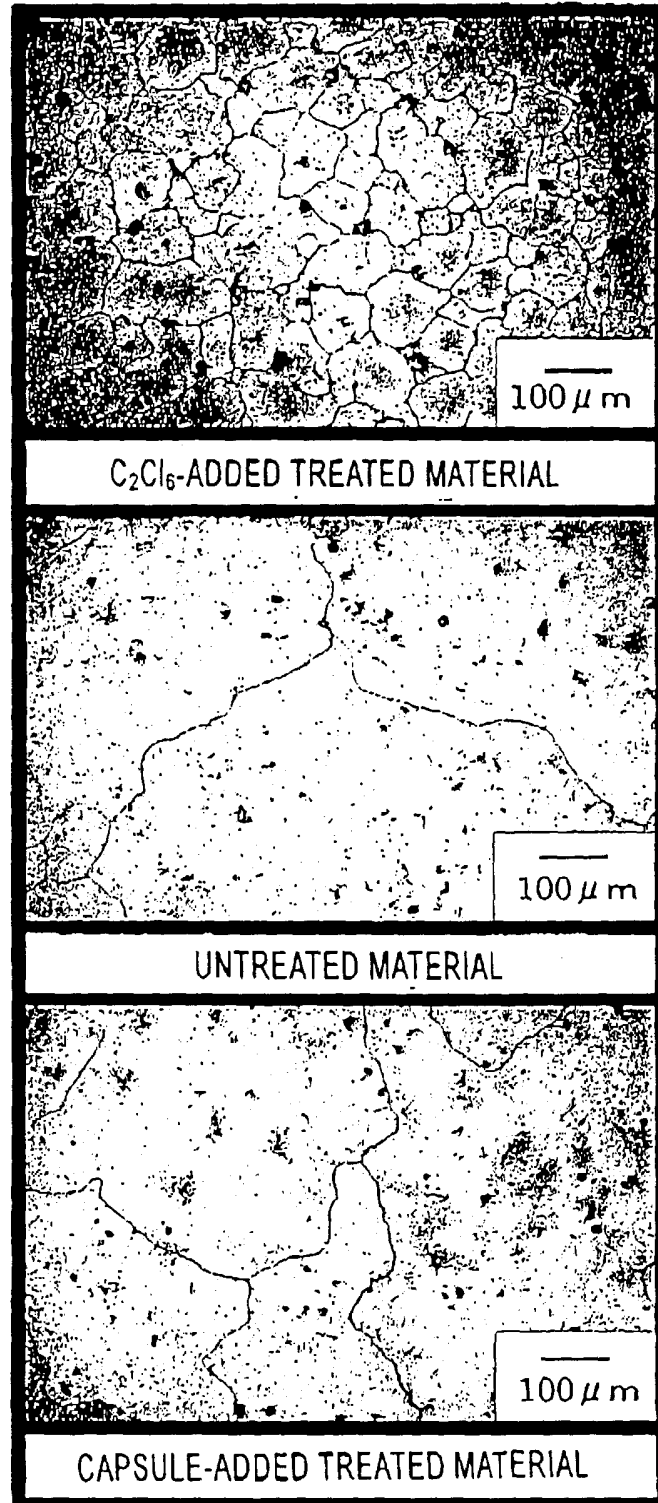


FIG. 6

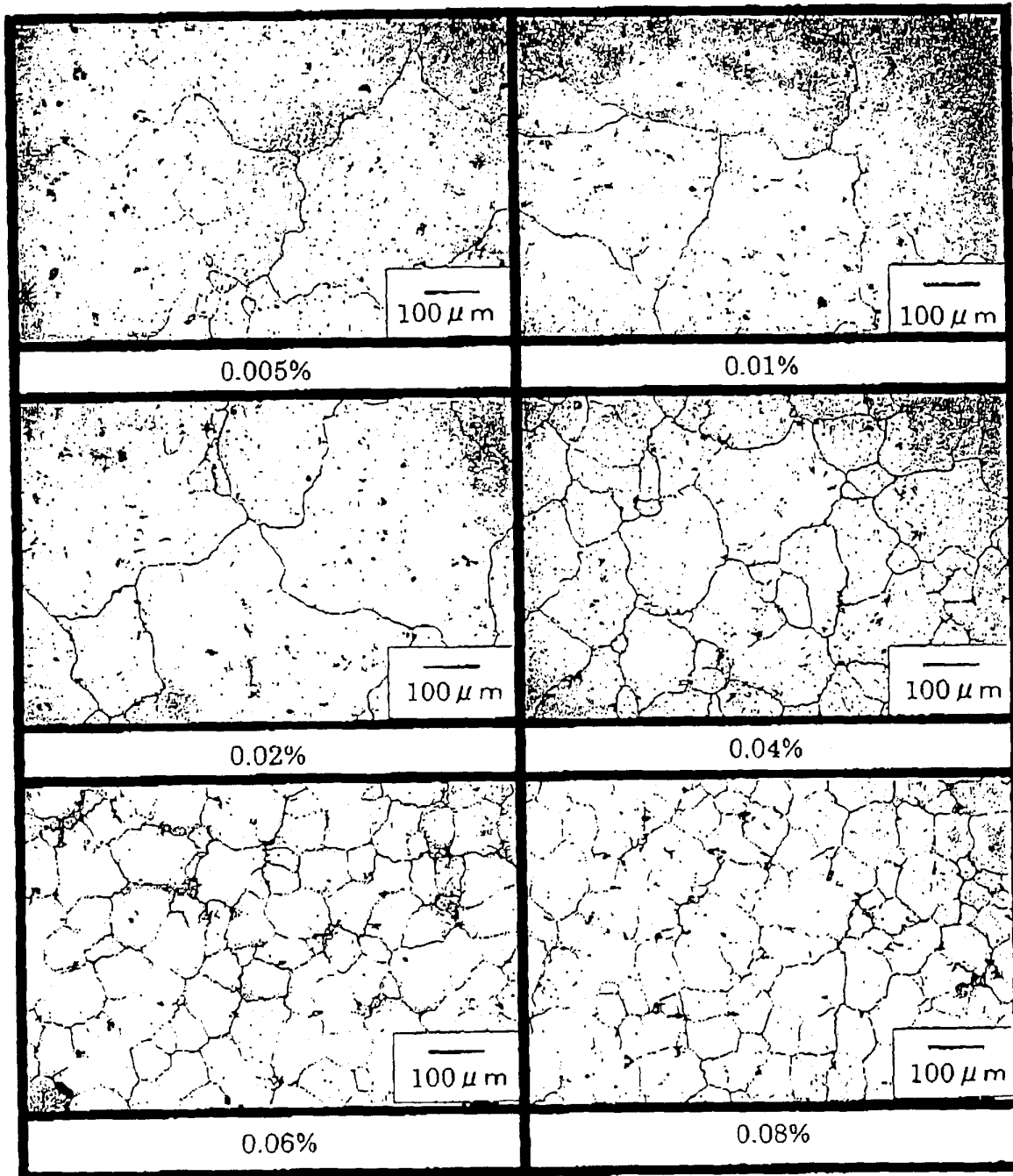


FIG. 7

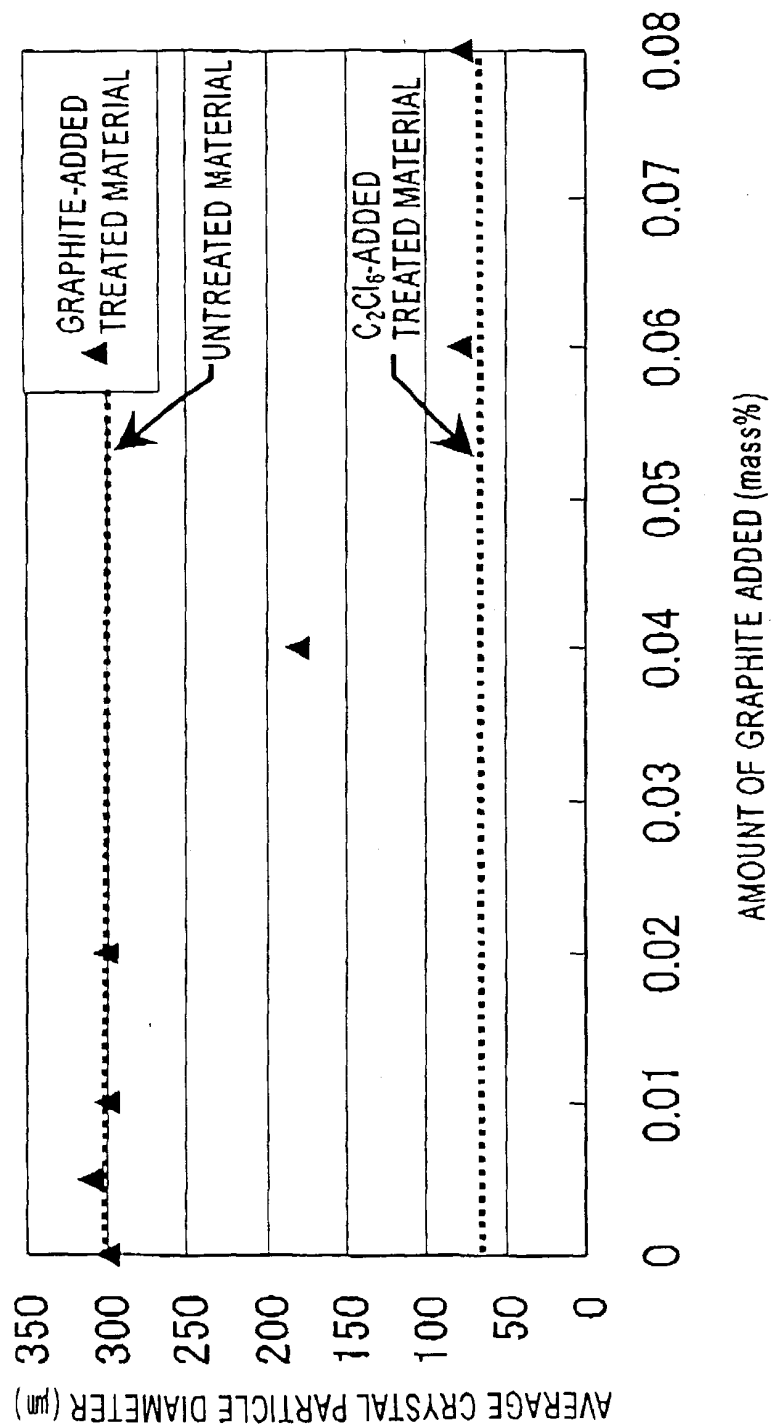


FIG. 8

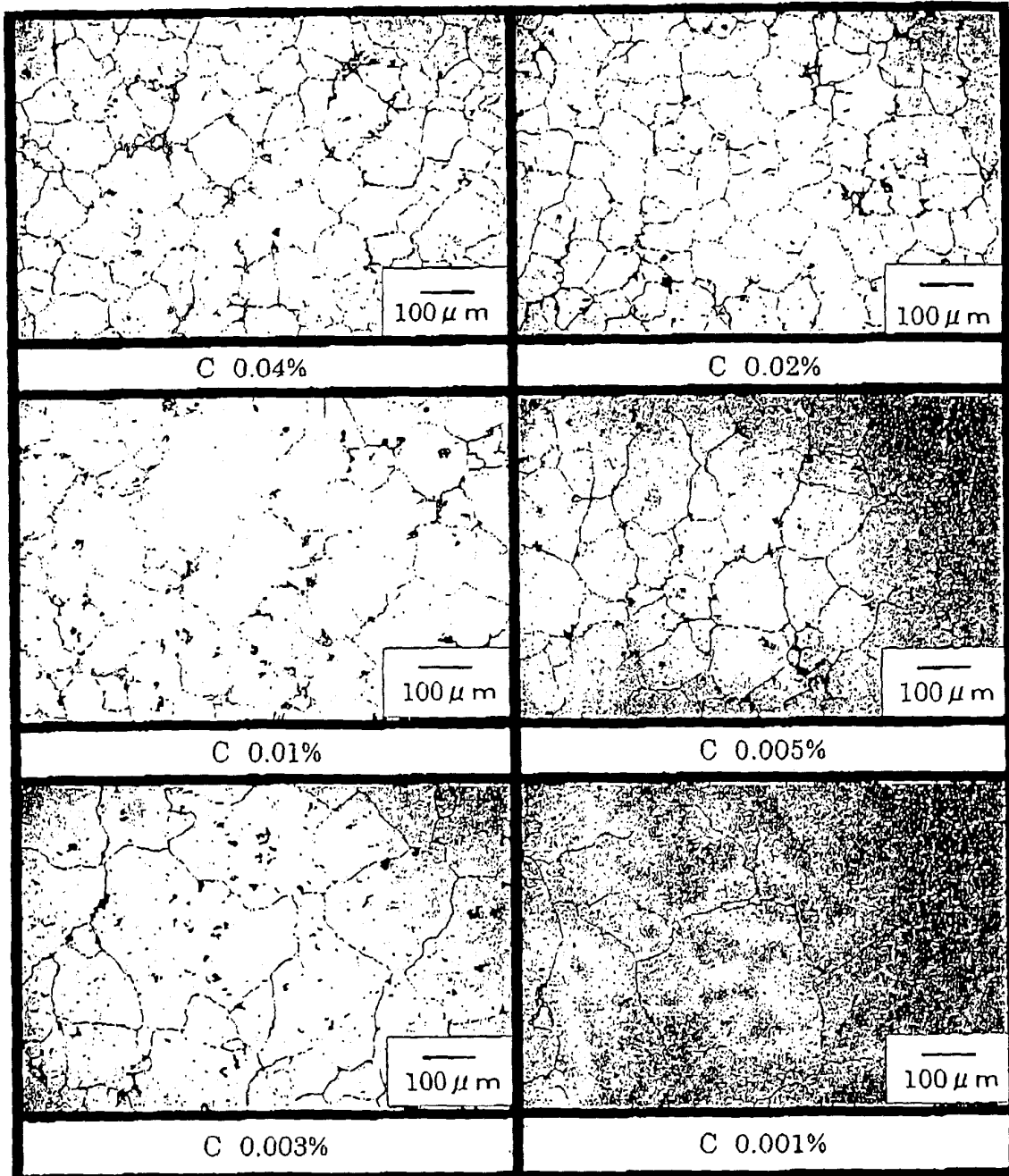


FIG. 9

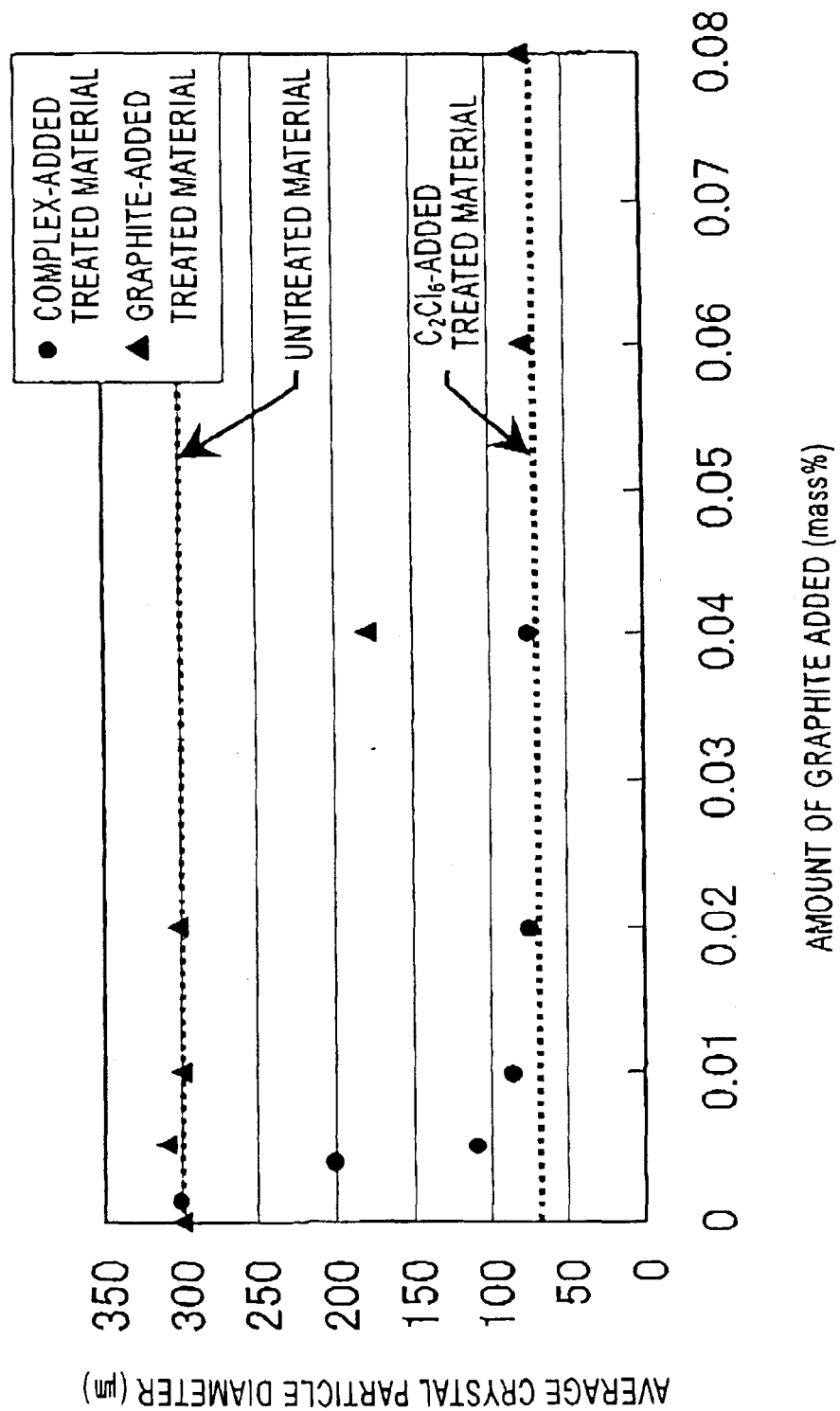


FIG. 10

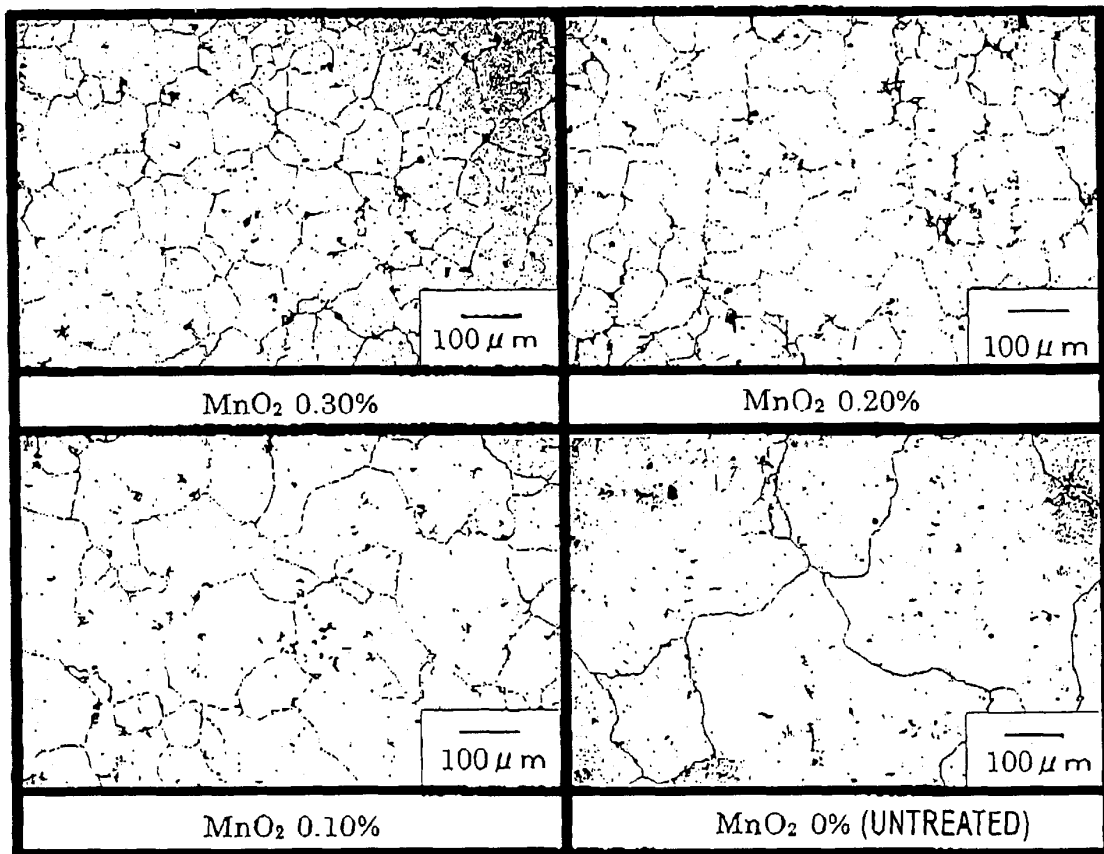


FIG. 11

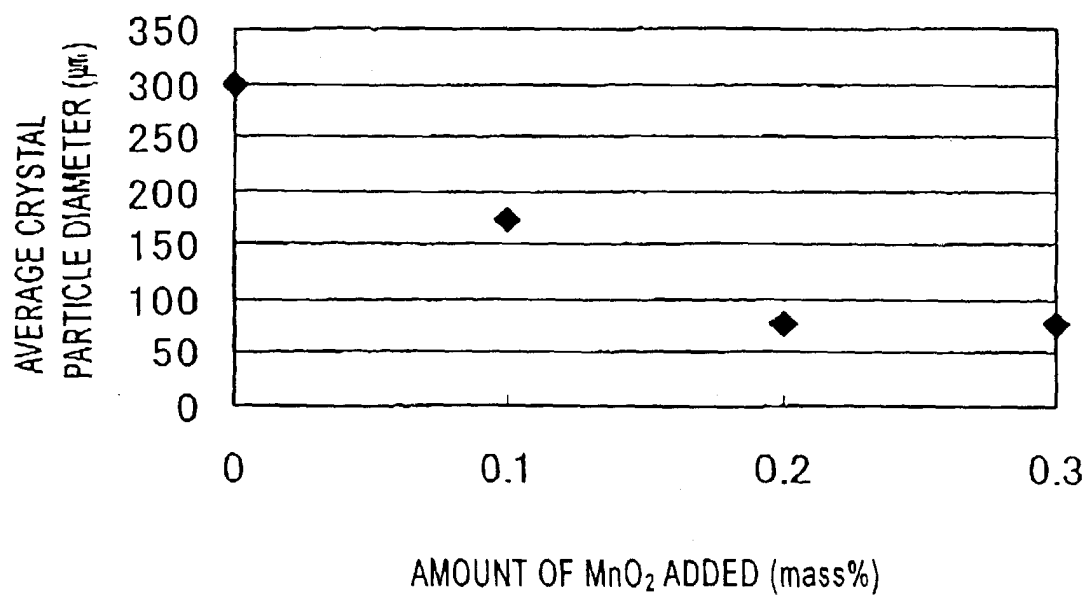


FIG. 12

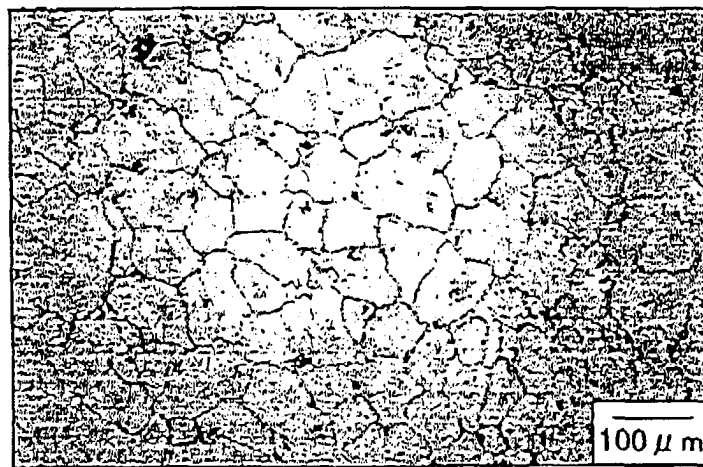


FIG. 13

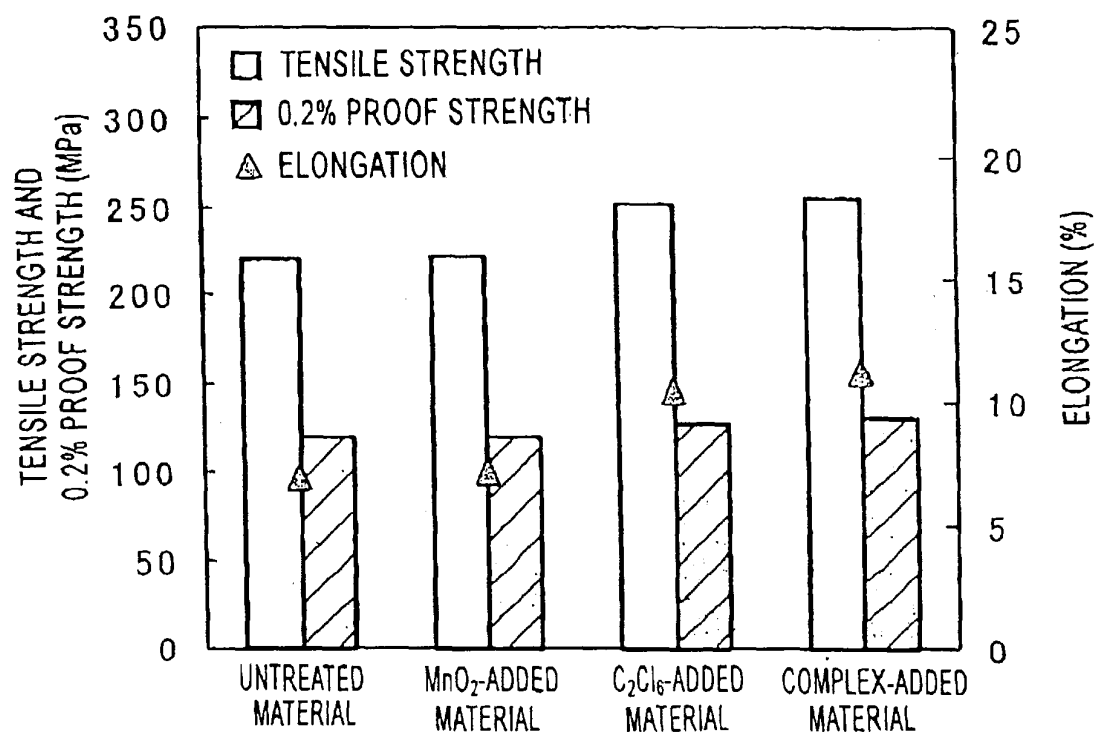
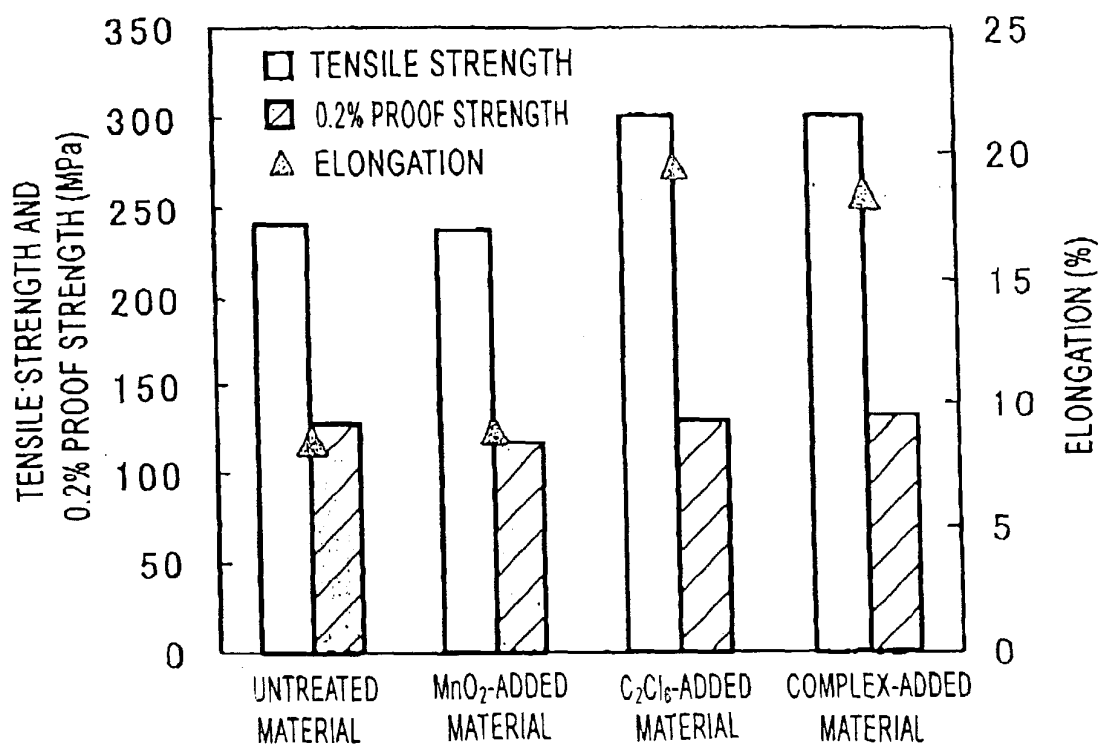


FIG. 14





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 04 25 2380

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.7)
A	EP 1 281 780 A (MIYAZAKI KEIICHI ; MOTEGI TETSUICHI (JP); SEIKO IDEA CT CO LTD (JP); T) 5 February 2003 (2003-02-05) * claims 1-4 * * examples 1,2 *	1-6	C22C1/00 C22C1/02 C22B9/10 C22C23/02
A	GB 2 022 138 A (MAGNESIUM ELEKTRON LTD) 12 December 1979 (1979-12-12) * claims 1-10 * * examples 1-9 *	1-6	
A	GB 421 904 A (CIE GENERAL D ELECTRO METALLUR) 2 January 1935 (1935-01-02) * claims 1,2 * * page 1, line 1 - page 3, line 113 *	1-6	
A	EP 0 575 796 A (NORSK HYDRO TECHNOLOGY) 29 December 1993 (1993-12-29) * claims 1-10 * * examples 1-7 *	1-6	
A	GB 608 942 A (BASIC MAGNESIUM INC) 23 September 1948 (1948-09-23) * claims 1-15 * * examples I,II *	1-6	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C22C C22B
A	PATENT ABSTRACTS OF JAPAN vol. 2002, no. 11, 6 November 2002 (2002-11-06) -& JP 2002 206153 A (NIPPON KINZOKU KAGAKU KK; ASAHI TEC CORP), 26 July 2002 (2002-07-26) * abstract *	1-6	
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 16 July 2004	Examiner Vlassi, E
CATEGORY OF CITED DOCUMENTS 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	

EPO FORM 1503 03 82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 04 25 2380

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

16-07-2004

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1281780	A	05-02-2003	JP 2003041331 A	13-02-2003
			CA 2396147 A1	30-01-2003
			EP 1281780 A1	05-02-2003
			US 2003019547 A1	30-01-2003
GB 2022138	A	12-12-1979	AU 520669 B2	18-02-1982
			AU 4735279 A	06-12-1979
			BE 876638 A1	17-09-1979
			BR 7903415 A	11-12-1979
			CA 1128783 A1	03-08-1982
			CH 639138 A5	31-10-1983
			DE 2921222 A1	06-12-1979
			FR 2427397 A1	28-12-1979
			IL 57417 A	15-05-1983
			IN 152252 A1	26-11-1983
			IT 1114041 B	27-01-1986
			JP 1388855 C	14-07-1987
			JP 55011191 A	25-01-1980
			JP 61054101 B	20-11-1986
			NL 7904276 A	04-12-1979
			NO 791631 A ,B,	03-12-1979
			SE 447130 B	27-10-1986
			SE 7904725 A	01-12-1979
			US 4239535 A	16-12-1980
			ZA 7902455 A	28-01-1981
GB 421904	A	02-01-1935	NONE	
EP 0575796	A	29-12-1993	AT 145014 T	15-11-1996
			CA 2097983 A1	11-12-1993
			DE 69305792 D1	12-12-1996
			DE 69305792 T2	15-05-1997
			EP 0575796 A1	29-12-1993
			JP 2939091 B2	25-08-1999
			JP 6073485 A	15-03-1994
			NO 932135 A ,B,	13-12-1993
			US 5501748 A	26-03-1996
GB 608942	A	23-09-1948	NONE	
JP 2002206153	A	26-07-2002	NONE	