



(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
11.05.2011 Bulletin 2011/19

(51) Int Cl.:
C22C 23/06 (2006.01) C22F 1/06 (2006.01)
C22F 1/00 (2006.01)

(21) Application number: **09800476.5**

(86) International application number:
PCT/JP2009/063452

(22) Date of filing: **22.07.2009**

(87) International publication number:
WO 2010/010965 (28.01.2010 Gazette 2010/04)

(84) Designated Contracting States:
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 SE SI SK SM TR
Designated Extension States:
AL BA RS

- **SOMEKAWA, Hidetoshi**
Tsukuba-shi
Ibaraki 305-0047 (JP)
- **SHOJI, Tetsuya**
Toyota-shi
Aichi 471-8571 (JP)
- **KATO, Akira**
Toyota-shi
Aichi 471-8571 (JP)

(30) Priority: **22.07.2008 JP 2008188397**

(71) Applicant: **National Institute for Materials Science**
Tsukuba-shi, Ibaraki 305-0047 (JP)

(74) Representative: **Kuhnen & Wacker**
Patent- und Rechtsanwaltsbüro
Prinz-Ludwig-Strasse 40A
85354 Freising (DE)

(72) Inventors:
• **MUKAI, Toshiiji**
Tsukuba-shi
Ibaraki 305-0047 (JP)

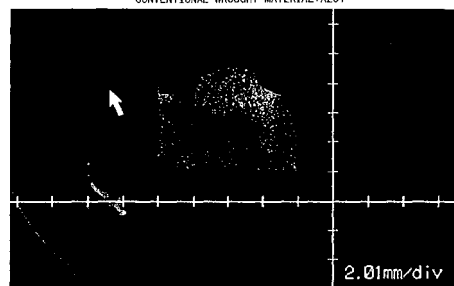
(54) **COLD-WORKED Mg-BASE ALLOY PRODUCT**

(57) The present invention has as its object to provide an Mg-based alloy cold worked member which can remarkably lower the load weight required for cold plastic working and enables practical usage of the same. The present invention is an Mg-based alloy cold worked member obtained by cold working an Mg-based alloy to form it into a predetermined shape, **characterized by** having a microstructure which includes crystal grains divided and made finer by cold working.

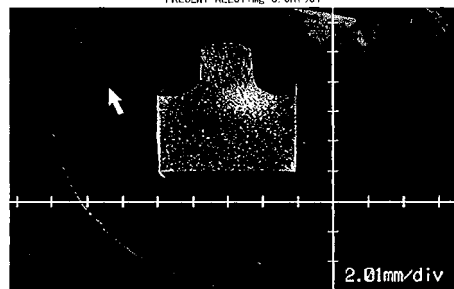
Fig.8

SHAPING EXAMPLE: TOP DIE EXTRUSION SPEED: 0.0003mm/sec
LOAD WEIGHT: 45KN (4.5tons)

CONVENTIONAL WROUGHT MATERIAL: AZ31



PRESENT ALLOY: Mg-0.6Al-9%Y



Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to an Mg-based alloy to which yttrium or another lanthanoid-series rare earth element has been added and relates to an Mg-based alloy which can be easily plastically worked.

BACKGROUND ART

10 **[0002]** In a conventional Mg-based alloy of this type, the plastic workability in the cold working temperature (room temperature or so temperature) region was difficult, so while utilization for light weight materials for structural use etc. has been desired, realization has been difficult.

SUMMARY OF INVENTION

15 **[0003]** The present invention has as its object to provide an Mg-based alloy cold worked member which can remarkably lower the load weight required for cold plastic working and enables practical usage of the same.

[0004] The present invention provides an Mg-based alloy cold worked member obtained by cold working an Mg-based alloy to form it into a predetermined shape, characterized by having a microstructure which includes crystal grains divided and made finer by cold working.

[0005] In the Mg-based alloy worked member of the present invention, preferably the Mg-based alloy forming the member has one or more types of lanthanoid-series rare earth elements added to it.

[0006] Further, in the Mg-based alloy worked member of the present invention, preferably the average value of the crystal grain size is 30 μm or less.

25 **[0007]** Due to the above such characteristic internal structure, the anisotropy of deformation normally observed in conventional wrought alloys such as the AZ31 alloy is eliminated and the demerit that, for example, the yield stress when a tensile load acts, that is, the plastic deformation starting stress, having to be 1.2 to 1.4 times the plastic deformation starting stress when a compressive load acts is eliminated.

30 **[0008]** The present alloy has isotropy of deformation. Equal deformation in all directions is exhibited for a constant load. At the same time, the load which is required for deformation work does not depend on the load either and is equal.

BRIEF DESCRIPTION OF DRAWINGS

[0009]

35 FIG. 1 is a high resolution transmission type electron microscope photograph of the internal microstructure forming the present alloy (Example 4).

FIG. 2 is a high resolution transmission type electron microscope photograph by the Z contrast method of the internal microstructure forming the present alloy (Example 4).

40 FIG. 3 includes a top figure of a photograph which shows the locations of presence of yttrium atoms, observed by a 3D atom probe, by dots for the present alloy (Example 4). The bottom figure is a schematic view based on the distribution of the top figure and shows the regions where yttrium atoms are segregated at a high concentration by gray color contour figures.

45 FIG. 4 is a graph showing the compressive nominal stress-nominal strain relationship of the present alloy for the Mg-0.6at%Y alloy of Example 4.

FIG. 5 is a graph for the case where obtaining a test piece from a member, in the compression test shown in FIG. 4, given a nominal strain of 0.4 in a direction parallel to extrusion, that is, compressive deformation until 60% of the initial height, and performing a static compression test in the same way as the case of FIG. 4.

FIG. 6 is a longitudinal cross-sectional view of a die set for evaluation of cold workability.

50 FIG. 7 is a graph using a jig shown in FIG. 6 for evaluating the cold workability. It shows the results for the materials shown in Example 1, Example 2, Example 4, and Comparative Example 1.

FIG. 8 is a photograph of the cross-section of a sample after shaping. It shows the results of an extrusion speed of 0.0003 mm/sec and a 4.5 ton load.

55 FIG. 9 is a photograph of the cross-section of a sample after shaping. Here, it shows the results of an extrusion speed of 0.03 mm/sec and a 4.5 ton load. The top figure shows the example of an AZ31 alloy, while the bottom figure shows the example of an Mg-0.6at%Y alloy of the present alloy.

FIG. 10 shows the changes in distribution of orientation of crystal grains before and after compressive deformation of a material of Mg-0.6at%Y extruded at 425°C and held at 400°C for 24 hours and the average crystal grain size

(d). Here, it shows the internal microstructure formed before shaping and after 4% (nominal strain 0.04), 15% (nominal strain 0.15), and 25% (nominal strain 0.25) deformation.

FIG. 11 shows the internal microstructure formed after deformation of a material similar to FIG. 10 by 45% (nominal strain 0.45) and average crystal grain size (d).

FIG. 12 is an enlarged view of the internal microstructure formed after deformation of a material similar to FIG. 10 by 15% (nominal strain 0.15).

FIG. 13 shows the change in microstructure formed inside a material after cold working of a comparative material, obtained by extruding the conventional material of an AZ31 alloy at 250°C, then holding it at 400°C for 24 hours, by the method shown in FIG. 6 by a top die at a speed of 0.0003 mm/sec.

FIG. 14 shows the change in microstructure formed inside a material after cold working of a material, obtained by extruding Mg-0.6at%Y at 320°C, then holding it at 400°C for 24 hours, by the method shown in FIG. 6 by a top die at a speed of 0.0003 mm/sec.

FIG. 15 shows the change in microstructure formed inside a material after cold working of a material, obtained by extruding Mg-0.1at%Y at 290°C, then holding it at 400°C for 24 hours, by the method shown in FIG. 6 by a top die at a speed of 0.0003 mm/sec.

FIG. 16 shows, as an example of cold working, the internal microstructure of a boss-shaped protrusion formed after cold working a material, obtained by extruding Mg-0.1at%Y at 290°C and holding it at 400°C for 24 hours, and a material, obtained by extruding Mg-0.3at%Y at 300°C and holding it at 400°C for 24 hours, by the method shown in FIG. 6 by a top die at a speed of 0.0003 mm/sec and 3.0 mm/sec.

FIG. 17 shows, as an example of cold working, the internal microstructure of a boss-shaped protrusion formed after cold working a material, obtained by extruding Mg-0.1at%Y at 290°C and holding it at 400°C for 24 hours, and a material, obtained by extruding Mg-0.3at%Y at 300°C and holding it at 400°C for 24 hours, by the method shown in FIG. 6 by a top die at a speed of 3.0 mm/sec.

FIG. 18 shows, as an example of cold working, the internal microstructure of a boss-shaped protrusion formed after cold working a material, obtained by extruding Mg-0.1at%Y at 290°C and holding it at 400°C for 24 hours, by the method shown in FIG. 6 by a top die at a speed of 0.0003 mm/sec.

FIG. 19 shows the hardness of a protrusion formed after shaping by the cold working method described in FIG. 6 in comparison with parts with little amounts of deformation.

FIG. 20 shows, as a comparative example, a nominal stress-nominal strain curve (top figure) obtained when causing compressive deformation of a material obtained by extruding pure magnesium at 328°C and holding it at 400°C for 24 hours and a nominal stress-nominal strain curve obtained when causing compressive deformation of a compression test piece, obtained by stopping deformation at a nominal strain of 0.14, then machining again, in parallel and perpendicular directions to the extrusion.

FIG. 21 shows, as an example, a nominal stress-nominal strain curve (top figure) obtained when causing compressive deformation of a material obtained by extruding Mg-0.3at%Y at 300°C and holding it at 400°C for 24 hours and a nominal stress-nominal strain curve obtained when causing compressive deformation of a compression test piece, obtained by stopping deformation at a nominal strain of 0.4, then machining again, in parallel and perpendicular directions to the extrusion.

FIG. 22 shows, as an example, a nominal stress-nominal strain curve (top figure) obtained when causing compressive deformation of a material obtained by extruding Mg-1.0at%Y at 425°C and holding it at 400°C for 24 hours and a nominal stress-nominal strain curve obtained when causing compressive deformation of a compression test piece, obtained by stopping deformation at a nominal strain of 0.4, then machining again, in parallel and perpendicular directions to the extrusion.

FIG. 23 shows, as an example, a nominal stress-nominal strain curve (top figure) obtained when causing compressive deformation of a material obtained by extruding Mg-0.3at%Yb at 300°C and holding it at 450°C for 24 hours and a nominal stress-nominal strain curve obtained when causing compressive deformation of a compression test piece, obtained by stopping deformation at a nominal strain of 0.4, then machining again, in parallel and perpendicular directions to the extrusion.

FIG. 24 shows, as an example, a nominal stress-nominal strain curve (top figure) obtained when causing compressive deformation of a material obtained by extruding Mg-0.3at%Gd at 300°C and holding it at 450°C for 24 hours and a nominal stress-nominal strain curve obtained when causing compressive deformation of a compression test piece, obtained by stopping deformation at a nominal strain of 0.35, then machining again, in parallel and perpendicular directions to the extrusion.

FIG. 25 shows, as a comparative example, the crystal grain structure of a material obtained by extruding Mg-0.6at%Y at an extrusion ratio of 25:1 and a temperature of 320°C. The black lines in the figure show the boundaries of a crystal orientation difference of 5° or more as crystal grain boundaries.

FIG. 26 shows the results when taking test pieces in the parallel and perpendicular directions of extrusion from the material obtained by extrusion of Mg-0.6at%Y at an extrusion ratio of 25:1 and temperature of 320°C shown as a

comparative example in FIG. 25 and testing them by a compression test at room temperature.

DESCRIPTION OF EMBODIMENTS

[0010] In a preferred embodiment of the present invention, the Mg-based alloy has an alloy microstructure which is homogeneous as a whole in $1\ \mu\text{m}^3$ units and has high Y concentration parts of average diameters of 2 to 50 nm dispersed irregularly in $1\ \mu\text{m}^3$.

[0011] In a still more preferable embodiment of the present invention, the Mg-based alloy has high Y concentration parts of high concentrations of 1.5 times or more the Y concentration in $1\ \mu\text{m}^3$ units.

[0012] The internal structure of the material of the present invention is characterized in that regions in which the yttrium atoms are present in a concentration higher by 50% or more of the average concentration in the material, that is, a 1.5 times or higher concentration, form sizes of average diameters of 2 nm to 50 nm and, furthermore, these high concentration regions are distributed in the crystal grains of the material at intervals of 2 nm to 50 nm.

[0013] Further, the yttrium atoms distributed in a high concentration do not form intermetallic compounds with the matrix of the magnesium atoms, that is, a regular structure, but form a high concentration, but random distribution.

[0014] The material of the present invention is characterized in that, by being cold worked at a nominal strain of 0.15 or more (as absolute value of equivalent strain, 0.17 or more), its internal crystal microstructure is divided and made finer whereby it is given crystal grain sizes of average values of 30 μm or less.

[0015] The Mg-based alloy of the present invention can be used to produce any long bars, sheet materials, or block materials. It becomes possible to secure cold workability of magnesium, which had been considered difficult in the past. It is expected to contribute much to all sorts of applications as a light weight structural material.

EXAMPLES

<Preparation of Alloy>

[0016] Yttrium (Y) and pure magnesium (Mg) (purity 99.95%) were completely melted in an argon atmosphere and cast in iron casting molds to prepare nine types of Mg-Y alloys having Y contents of 0.1 at%, 0.3 at%, 0.6 at%, 1.0 at%, 1.2 at%, 1.5 at%, 2.0 at%, 2.2 at%, and 3.0 at%. Table 1 shows these as Examples 1 to 8 and Comparative Example 1.

[0017] The obtained cast alloys were held at a temperature of 500°C for 24 hours in a furnace (air atmosphere), then water cooled for solution treatment.

[0018] After this, they were machined to columnar materials of diameters of 40 mm and lengths of 70 mm.

[0019] These columnar materials were held in containers (in the air) held at the extrusion temperatures shown in Table 1 for 30 minutes, then extruded at an extrusion ratio of 25:1 as strong strain hot working. The average equivalent plastic strain, found from the rate of reduction of cross-section, was 3.7.

[0020] The extruded materials were held isothermally in furnaces of a temperature of 300 to 550°C for 24 hours, then were air cooled outside the furnaces. For the extrusion temperatures, the temperatures shown in Table 1 were used. The average recrystallized grain size (μm), tensile yield stress (A), compressive yield stress (B), yield stress ratio (B/A), and compressive strain at break were measured. The results are shown together in Table 1.

Table 1

Sample No.	Alloy (at%)	Extrusion temp. (°C)	Average recrystallized grain size (μm)	Tensile yield stress (A) (MPa)	Compressive yield stress (B) (MPa)	Yield stress ratio (B/A)	Compressive strain at break
1	Mg-0.1Y	310	80	87	56	0.64	0.49
2	Mg-0.3Y	310	50	88.2	59	0.67	0.5
3	Mg-0.3Y	310	264	53	44	0.83	0.5
4	Mg-0.6Y	425	44	86	77	0.9	0.51
5	Mg-0.67Y	320	17	97	95	0.98	0.5
6	Mg-0.67Y	320	49	89	76	0.85	0.5
7	Mg-0.67Y	320	174	64	52	0.81	0.48
8	Mg-1.2Y	340	17	119	115	0.97	0.51

(continued)

Sample No.	Alloy (at%)	Extrusion temp. (°C)	Average recrystallized grain size (μm)	Tensile yield stress (A) (MPa)	Compressive yield stress (B) (MPa)	Yield stress ratio (B/A)	Compressive strain at break
9	Mg-1.2Y	340	29	88	87	0.99	0.5
10	Mg-1.2Y	340	193	78	70	0.9	0.41
11	Mg-1.5Y	360	33	100	101	1.01	0.47
12	Mg-1.5Y	360	164	94	91	0.97	0.35
13	Mg-2.0Y	420	37	152.8	144	0.94	0.37
14	Mg-2.2Y	425	240	117	118	1.01	0.32
15	Mg-3.0Y	450	148	156	154	0.99	0.28
	Comp. ex.						
1	AZ31 alloy	250	40		115		0.12

[0021] FIG. 1 is a high resolution transmission type electron microscope photograph of the internal microstructure forming the present alloy. The fine dots forming FIG. 1 show the positions of present of the component atoms. This photograph is taken from a direction parallel to a certain crystal plane of the present alloy (Example 4), so that majority of the points, that is, atoms, are arranged on a certain line in the structure.

[0022] However, there are partial locations where the arrangement is disturbed. This is because yttrium atoms with relatively large atomic radii are dispersed among the magnesium matrix atoms and distort the array units, that is, the lattice.

[0023] Furthermore, due to the plurality of yttrium atoms being irregularly concentrated, the lattice distortion becomes remarkable. As a result, regions of remarkable lattice distortion, such as shown by the white broken line circles or the white broken line ellipses in the figure, are formed.

[0024] Therefore, the present alloy is characterized in that the yttrium atoms do not form regular structures with the magnesium matrix atoms, that is, so-called "intermetallic compounds", but form high concentration regions of yttrium.

[0025] The sizes of the lattice distorted regions can be measured from an electron micrograph such as shown in the illustration. Based on the results of measurement, it was confirmed that the lattice distorted regions had an average diameter size of 2 to 50 nm and dispersion interval of 2 to 50 nm. However, in some regions, formation of unavoidable intermetallic compounds was observed, so the formation of high concentration regions where over half of the yttrium atoms are distributed at random is made the characterizing feature of the present alloy.

[0026] Note that the concentration of yttrium can be made a range of 0.1 at% to 3.0 at%.

[0027] The method of production of the material comprises production of an alloy having a predetermined yttrium concentration by casting etc., extrusion etc. to impart hot an equivalent plastic strain of 1 or more to the material, then holding it isothermally at 300 to 550°C in range.

[0028] FIG. 2 is a high resolution transmission type electron microscope photograph of the internal microstructure forming the present alloy (Example 4). This photograph uses the Z contrast method to show the yttrium atoms, which are heavier atoms than magnesium matrix atoms, as dots of different contrasts. For example, the white broken line circles or white broken line ellipses in the figure show regions where large numbers of yttrium atoms are concentrated.

[0029] The sizes and dispersion intervals of these regions match those of the lattice distorted regions shown in FIG. 1, so it is clear that the characterizing structure of the present alloy is formed by the yttrium atoms being concentrated at a high concentration and at random.

[0030] The top figure of FIG. 3 is a photograph which shows the locations of presence of yttrium atoms observed by a 3D atom probe by dots for the present alloy (Example 4). The bottom figure is a schematic view based on the distribution of the top figure and shows the regions where yttrium atoms are segregated at a high concentration by gray color contour figures.

[0031] Here, the results are shown relating to an alloy containing 0.6 at% of yttrium as an example of the alloy.

[0032] The average concentration of the yttrium in the illustrated alloy is 0.6 at%. Here, the size and dispersion interval of regions of 1.0 at% or more concentration regions, that is, regions where the concentrations are 1.67 times or more of the average concentration, are shown.

[0033] The sizes of the concentration regions are 5 to 15 nm. The intervals between regions are also 5 to 15 nm.

Results similar to the strain regions of FIG. 1 and the high concentration regions of FIG. 2 are shown.

[0034] FIG. 4 is a graph showing the compressive nominal stress-nominal strain relationship of the present alloy for the Mg-0.6at%Y alloy of Example 4. As the directions of the compression tests, three are selected: one parallel to the extrusion direction of the extruded material (180°), one perpendicular to it (90°), and one between the two (45°).

[0035] The yield stress, that is, the plastic deformation start stress, is about 60 MPa. By the later work hardening and, furthermore, by a strain of about 0.12, the gradient of work hardening becomes gentler. Up to a nominal strain of 0.43 to 0.5 or so, a state free from breakage is maintained. As clear from a comparison of the results of deformation in three directions, it is learned that there is almost no dependency of deformation on direction.

[0036] The non-directional dependent compressive deformation performance such as shown above is a property not exhibited by the conventional wrought materials of AZ31 alloy etc.

[0037] FIG. 5 is a graph for the case where obtaining a test piece from a member, in the compression test shown in FIG. 4, given a nominal strain of 0.4 in a direction parallel to extrusion, that is, compressive deformation until 60% of the initial height, and performing a static compression test in the same way as the case of FIG. 4.

[0038] As a result, it was learned that a material given a nominal compressive strain of 0.4 as an initial strain increases in deformation start stress to about 200 MPa. Further, as clear from the test results, the magnitude of the deformation start stress and the ratio of the subsequent work hardening are similar regardless of the compression test direction.

[0039] Further, in a material made to deform in the same direction as the test direction of FIG. 4, it was learned that the nominal strain at break of a large value of 0.37 was obtained.

[0040] From the findings shown in the above FIG. 4 and FIG. 5, it was suggested that the present alloy has plastic workability at room temperature, that is, cold workability, and, furthermore, the mechanical properties after plastic working are excellent as well.

[0041] To clarify the cold workability of the present alloy, the die set such as shown in FIG. 6 was used to evaluate the plastic workability.

[0042] A test piece before deformation was made a columnar shape of a diameter of 8 mm and a height of 6 mm.

This was set at a bottom die of tool steel having a columnar cross-section hole of the same diameter. After that, the top die, which has a columnar cross-section hole of a diameter of 3 mm at the center axis and an R part of a radius of 1.5 mm at the shoulders, was brought into contact with the top surface of the test piece. The top die was made to move from the top to the bottom of the figure so as to make the test piece constrained by the bottom die plastically flow along the center hole provided in the top die to thereby confirm the shapeability. Note that the surfaces of the test piece and die were coated with a lubricant of silicone grease.

[0043] In the process of the shaping test, the load weight required for shaping and the amount of extrusion by the top die were measured and used as indicators of shapeability.

[0044] If the shapeability of the material is sufficient, a boss of the same diameter as the top die such as shown in FIG. 6 is formed into a protruding shape, so from the observation of the cross-section after working, it is possible to directly confirm the shapeability and any cracking along with working.

[0045] FIG. 7 is a graph using a jig shown in FIG. 6 for evaluating the cold workability.

[0046] The results are shown using, as the test pieces, as examples of the present alloy, the Mg-0.1at%Y of Example 1, the Mg-0.3at%Y of Example 2, the Mg-0.6at%Y of Example 4, and, as Comparative Example 1, an AZ31 alloy under the same conditions.

[0047] Here, as the extrusion speeds of the top die, 0.0003 and 0.03 mm/sec were selected.

[0048] Note that, in the present test, the maximum load given was made 4.5 ton (45 kN).

[0049] As clear from the relationship of the load and the amount of extrusion deformation, it is learned that the load required for shaping the present alloy to obtain the same shaping height is about 20 to 40% lower compared with the case of the conventional material of AZ31.

[0050] FIG. 8 is a photograph of the cross-section of a sample after shaping. It shows the results of an extrusion speed of 0.0003 mm/sec and a 4.5 ton load. The top figure shows the case of the AZ31 alloy shown in Comparative Example 1. The shaping height including the R part was 1.8 mm.

[0051] The bottom figure shows an example of the Mg-0.6at%Y alloy of the present alloy (Example 4). The shaping height was 3.7 mm. A shaping height of at least 2 times that of an AZ31 alloy was obtained. The shapeability of the present alloy was therefore confirmed.

[0052] FIG. 9 is a photograph of the cross-section of a sample after shaping. Here, it shows the results of an extrusion speed of 0.03 mm/sec and a 4.5 ton load. The top figure shows the case of the AZ31 alloy shown in Comparative Example 1. The shaping height, including the R part, was 1.4 mm. The bottom figure shows the Mg-0.6at%Y alloy of the present alloy (Example 4). The shaping height was 2.9 mm. A shaping height of at least 2 times that of an AZ31 alloy was obtained. The shapeability of the present alloy was therefore confirmed.

[0053] Below, further data showing deformation of the crystals will be used to clarify the state of the cold working and the reason why this increases the strength. Experiments will be used to clearly indicate the numerical limits at which these phenomena occur. Further, it is shown that similar phenomena occur for rare earth elements other than Y.

[0054] FIG. 10 shows the changes in distribution of orientation of crystal grains before and after compressive deformation of a material of Mg-0.6at%Y extruded at 425°C and held at 400°C for 24 hours and the average crystal grain size. Here, it shows the internal microstructure formed before shaping and after 4% (nominal strain 0.04), 15% (nominal strain 0.15), and 25% (nominal strain 0.25) deformation. In a material giving deformation of a nominal strain of 0.15 or more, compared with the material before deformation, the average crystal grain size becomes 30 μm or less, that is, becomes finer.

[0055] FIG. 11 shows the internal microstructure formed after deformation of a material similar to FIG. 10 by 45% (nominal strain 0.45). The boundary lines shown by the black lines in the figure show parts where the crystal orientation difference is 5 degrees or more as the crystal grain boundaries. Compared with the microstructure before deformation shown in FIG. 10, it is learned that the crystal grain size is made a finer 1/5 size.

[0056] FIG. 12 is an enlarged view of the internal microstructure formed after deformation of a material similar to FIG. 10 by 15% (nominal strain 0.15). The changes in crystal orientation on the lines shown by L and T in the figure are shown by the solid lines in the right figures. The locations where the density changes, for example, the parts shown by the white arrows in the figure, clearly show an increase of the orientation angle by 5 degrees from the bottom right graph. That is, the cold worked member of the present invention, by being cold worked, changes in orientation inside certain crystal grains. Along with the increase of the strain imparted, the difference in crystal orientation becomes greater. Finally, crystal grain boundaries are formed, whereby the crystal grains are divided and the average crystal grain size inside the material becomes finer, it is shown.

[0057] FIG. 13 shows the change in microstructure formed inside a material after cold working of a comparative material, obtained by extruding the conventional material of an AZ31 alloy at 250°C, then holding it at 400°C for 24 hours, by the method shown in FIG. 6 by a top die at a speed of 0.0003 mm/sec. At the center part D of the worked material, no division of the crystal grains is seen. Deformation twins are formed as a banded structure in an oblique direction.

[0058] FIG. 14 shows the change in microstructure formed inside a material after cold working of a material, obtained by extruding Mg-0.6at%Y at 320°C, then holding it at 400°C for 24 hours, by the method shown in FIG. 6 by a top die at a speed of 0.0003 mm/sec. At the center part D of the worked material, there is no formation of a banded structure in any specific direction such as deformation twins. New grain boundaries are formed in random directions, it is learned.

[0059] FIG. 15 shows the change in microstructure formed inside a material after cold working of a material, obtained by extruding Mg-0.1at%Y at 290°C, then holding it at 400°C for 24 hours, by the method shown in FIG. 6 by a top die at a speed of 0.0003 mm/sec. At the center part D of the worked material, there is no formation of a banded structure in any specific direction such as deformation twins. New grain boundaries are formed in random directions, it is learned.

[0060] FIG. 16 shows, as an example of cold working, the internal microstructure of a boss-shaped protrusion formed after cold working a material, obtained by extruding Mg-0.1at%Y at 290°C and holding it at 400°C for 24 hours, and a material, obtained by extruding Mg-0.3at%Y at 300°C and holding it at 400°C for 24 hours, by the method shown in FIG. 6 by a top die at a speed of 0.0003 mm/sec and 3.0 mm/sec.

[0061] FIG. 17 shows, as an example of cold working, the internal microstructure of a boss-shaped protrusion formed after cold working a material, obtained by extruding Mg-0.1at%Y at 290°C and holding it at 400°C for 24 hours, and a material, obtained by extruding Mg-0.3at%Y at 300°C and holding it at 400°C for 24 hours, by the method shown in FIG. 6 by a top die at a speed of 3.0 mm/sec. In the schematic view of deformation of FIG. 13, the microstructure of the part shown by D is shown. It is learned that by a working speed of a speed of 3.0 mm/sec, similar crystal grain refinement occurs.

[0062] FIG. 18 shows, as an example of cold working, the internal microstructure of a boss-shaped protrusion formed after cold working a material, obtained by extruding Mg-0.1at%Y at 290°C and holding it at 400°C for 24 hours, by the method shown in FIG. 6 by a top die at a speed of 0.0003 mm/sec. From the distribution chart of orientation of the microstructure after deformation, it is learned that the crystal grain structure becomes finer.

[0063] FIG. 19 shows that the hardness of a protrusion formed after shaping by the cold working method described in FIG. 6 increases in comparison with parts with little amounts of deformation. It is learned that refinement of the crystal grains due to cold working increases the strength.

[0064] FIG. 20 shows, as a comparative example, a nominal stress-nominal strain curve (top figure) obtained when causing compressive deformation of a material obtained by extruding pure magnesium at 328°C and holding it at 400°C for 24 hours and a nominal stress-nominal strain curve obtained when causing compressive deformation of a compression test piece, obtained by stopping deformation at a nominal strain of 0.14, then machining again, in parallel and perpendicular directions to the extrusion. The yield strength greatly differs and anisotropy of deformation can be confirmed.

[0065] FIG. 21 shows, as an example, a nominal stress-nominal strain curve (top figure) obtained when causing compressive deformation of a material obtained by extruding Mg-0.3at%Y at 300°C and holding it at 400°C for 24 hours and a nominal stress-nominal strain curve obtained when causing compressive deformation of a compression test piece, obtained by stopping deformation at a nominal strain of 0.4, then machining again, in parallel and perpendicular directions to the extrusion. It can be confirmed that the anisotropy of the yield strength is reduced.

[0066] FIG. 22 shows, as an example, a nominal stress-nominal strain curve (top figure) obtained when causing

compressive deformation of a material obtained by extruding Mg-1.0at%Y at 425°C and holding it at 400°C for 24 hours and a nominal stress-nominal strain curve obtained when causing compressive deformation of a compression test piece, obtained by stopping deformation at a nominal strain of 0.4, then machining again, in parallel and perpendicular directions to the extrusion. It can be confirmed that the anisotropy of the yield strength is reduced.

[0067] FIG. 23 shows, as an example, a nominal stress-nominal strain curve (top figure) obtained when causing compressive deformation of a material obtained by extruding Mg-0.3at%Yb at 300°C and holding it at 450°C for 24 hours and a nominal stress-nominal strain curve obtained when causing compressive deformation of a compression test piece, obtained by stopping deformation at a nominal strain of 0.4, then machining again, in parallel and perpendicular directions to the extrusion. It can be confirmed that the anisotropy of the yield strength and rate of work hardening is reduced.

[0068] FIG. 24 shows, as an example, a nominal stress-nominal strain curve (top figure) obtained when causing compressive deformation of a material obtained by extruding Mg-0.3at%Gd at 300°C and holding it at 450°C for 24 hours and a nominal stress-nominal strain curve obtained when causing compressive deformation of a compression test piece, obtained by stopping deformation at a nominal strain of 0.35, then machining again, in parallel and perpendicular directions to the extrusion. It can be confirmed that the anisotropy of the yield strength and rate of work hardening is reduced.

[0069] FIG. 25 shows, as a comparative example, the crystal grain structure of a material obtained by extruding Mg-0.6at%Y at an extrusion ratio of 25:1 and a temperature of 320°C. The black line in the figure shows the interface of a crystal orientation difference of 5° or more as a crystal grain boundary. Compared with the example shown in FIG. 11, in the cold worked microstructure of this comparative example, it is learned that the division is insufficient at the left part and the center part in the figure and that coarse crystal grain structures remain.

[0070] FIG. 26 shows the results when taking test pieces in the parallel and perpendicular directions of extrusion from the material obtained by extrusion of Mg-0.6at%Y at an extrusion ratio of 25:1 and temperature of 320°C shown as a comparative example in FIG. 25 and testing them by a compression test at room temperature. It is learned that the nominal strain at the time of break is 0.13 or less and that, while having a composition similar to the alloys of the working examples shown in FIG. 4 and FIG. 5, the cold workability is lower. Further, the rate of work hardening after yielding greatly differs depending on the direction in which the sample is taken. It is learned that the nominal stress right before breakage at the time of a compression test in a direction parallel to extrusion becomes a value close to two times that in the direction perpendicular to extrusion, so the anisotropy of deformation is strong.

INDUSTRIAL APPLICABILITY

[0071] According to the present invention, an Mg-based alloy cold worked member which can remarkably lower the load weight required for cold plastic working is provided and can be practically used.

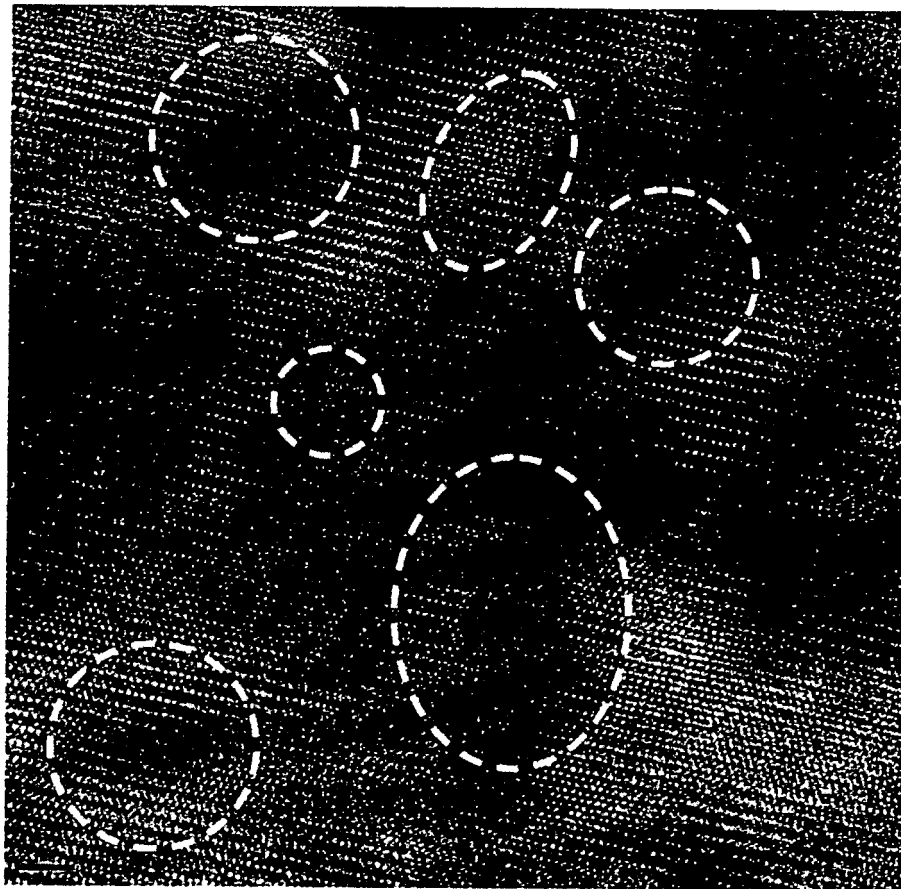
Claims

1. An Mg-based alloy cold worked member obtained by cold working an Mg-based alloy to form it into a predetermined shape, **characterized by** having a microstructure which includes crystal grains divided and made finer by cold working.
2. An Mg-based alloy worked member as set forth in claim 1, **characterized in that** the Mg-based alloy forming the member has one or more types of lanthanoid type rare earth elements added to it.
3. An Mg-based alloy worked member as set forth in claim 1 or 2, **characterized by** having an average value of its crystal grain size of 30 μm or less.
4. An Mg-based alloy worked member as set forth in claim 1 or 2, **characterized by** being given an equivalent strain by cold working at room temperature or other temperature of 150°C or less of, by absolute value, 0.17 (by nominal compressive strain, 0.15) or more.

Fig.1

REGIONS OF LATTICE DISTORTED IN MATERIAL OBSERVED BY HIGH
RESOLUTION TEM (TRANSMISSION TYPE ELECTRON MICROSCOPE)
(SHOWN BY WHITE BROKEN LINE CIRCLES IN FIGURE)

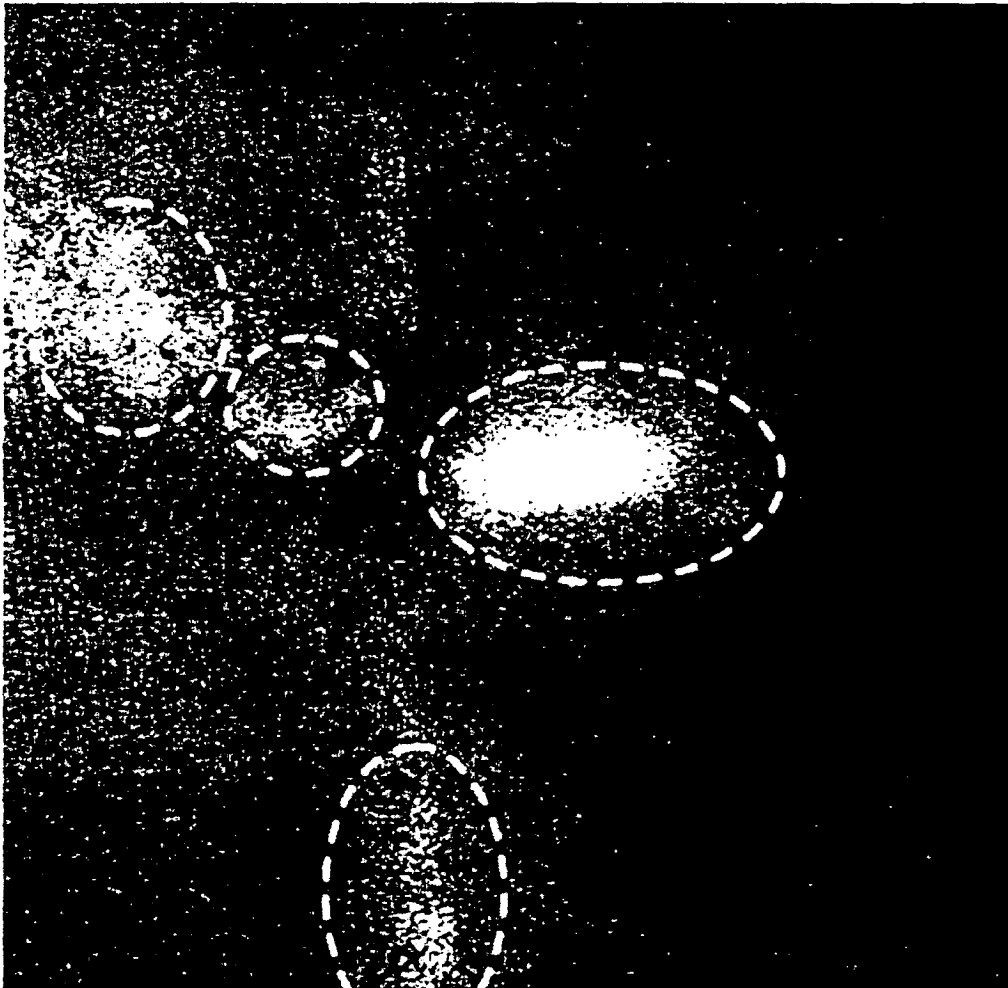
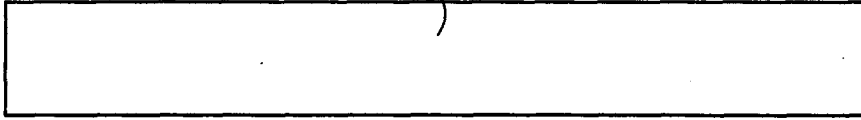
[EXAMPLE OF MATERIAL: Mg-0.6Y/425-400]



DISTORTED LATTICE
REGIONS PRESENT
AT INTERVALS OF
SEVERAL nm
TO 10nm

Fig.2

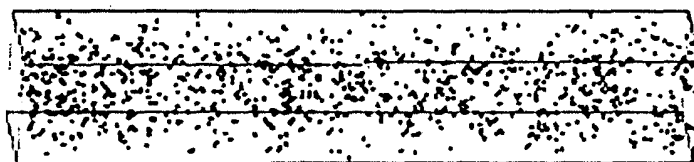
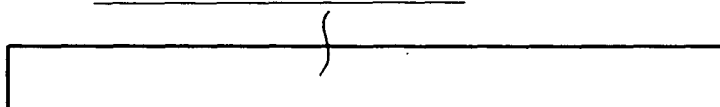
HIGH RESOLUTION TEM(TRANSMISSION TYPE ELECTRON MICROSCOPE)-Z contrast METHOD
(LOCATIONS WHERE YTTRIUM IS PRESENT IN HIGH CONCENTRATION SHOWN BY WHITE)



PRESENCE OF WHITE REGIONS IS DUE TO HIGH
CONCENTRATION SEGREGATION OF Y
→INDUCES DISLOCATION SLIP FROM BOTTOM
SURFACE TO NON-BOTTOM SURFACE

Fig.3

EXAMPLE OF OBSERVATION OF Y ATOM
DISTRIBUTION BY ATOM PROBE



[MAP OF Y ATOMS IN Mg-0.6AT% ALLOY]

(SIZE OF OBSERVED REGION:
 $10 \times 10.5 \times 60 \text{ nm}^3$)



[EXAMPLE OF INTERNAL MICROSTRUCTURE OF MATERIAL
(Mg-0.6at%Y ALLOY, HEAT TREATED MATERIAL), GRAY REGIONS:
REGIONS WHERE Y IS PRESENT IN HIGH CONCENTRATION(1.0at% OR MORE)]

Fig.4

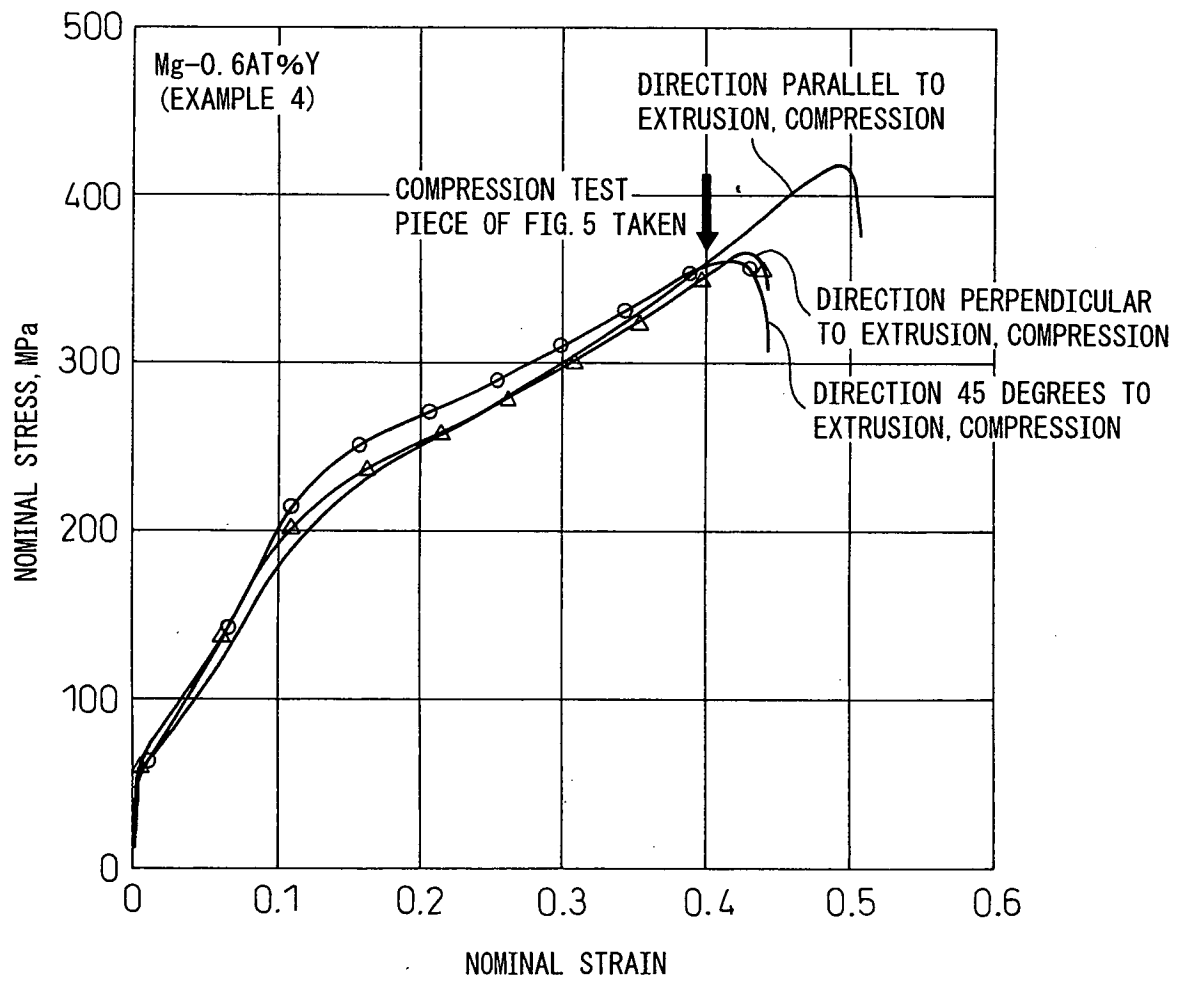


Fig.5

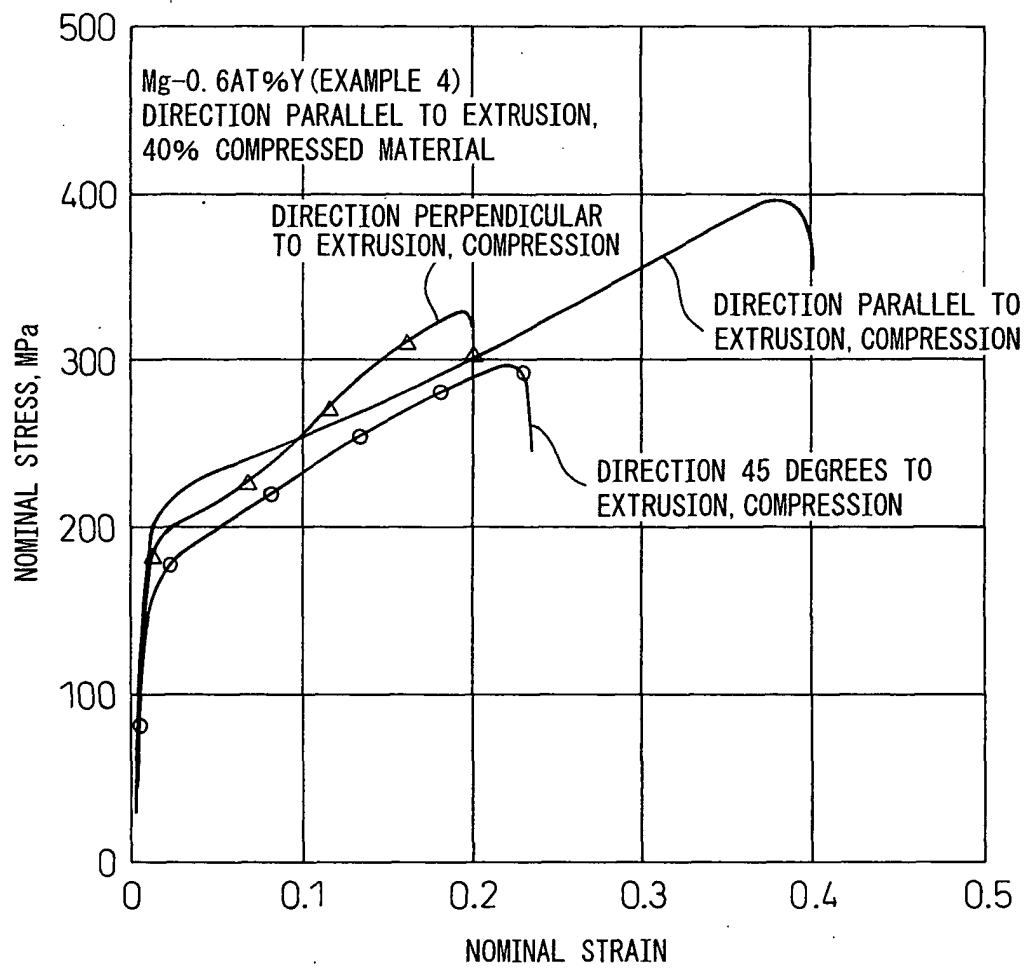


Fig.6

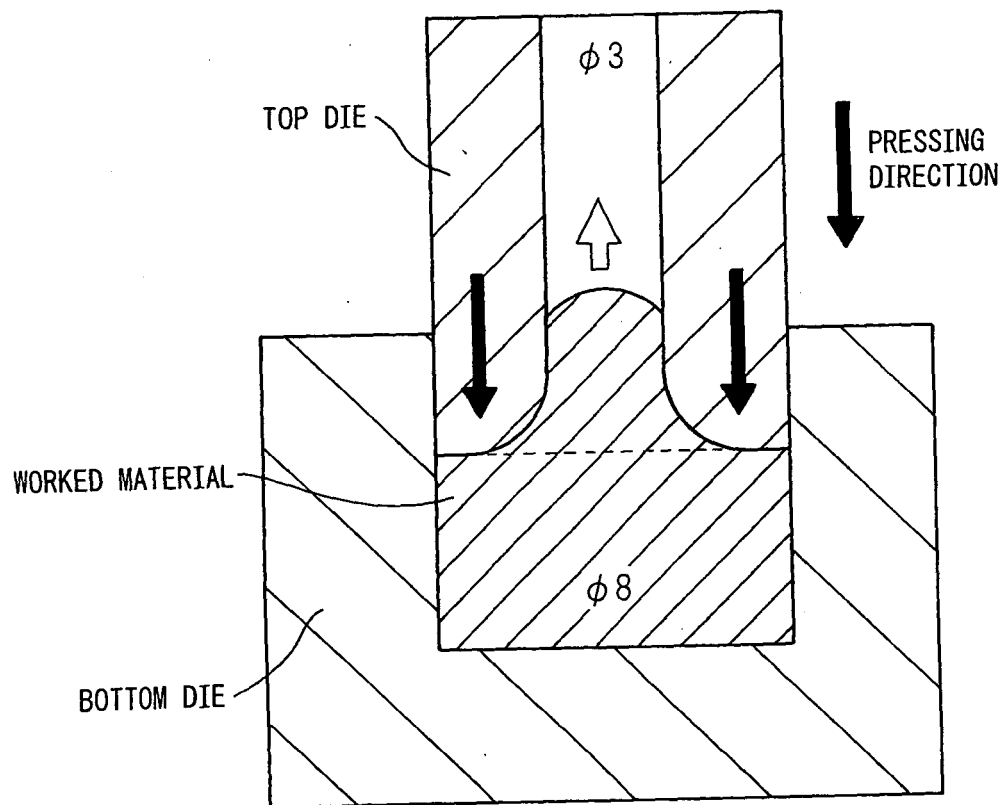


Fig.7

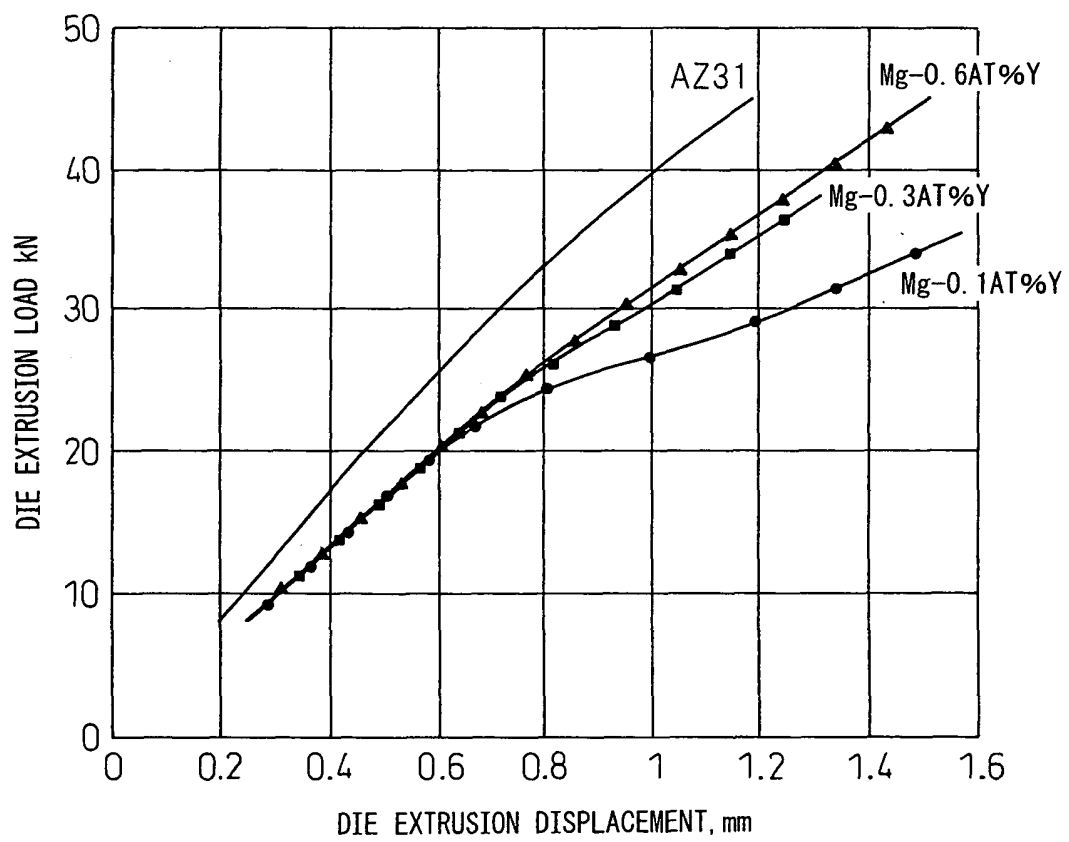
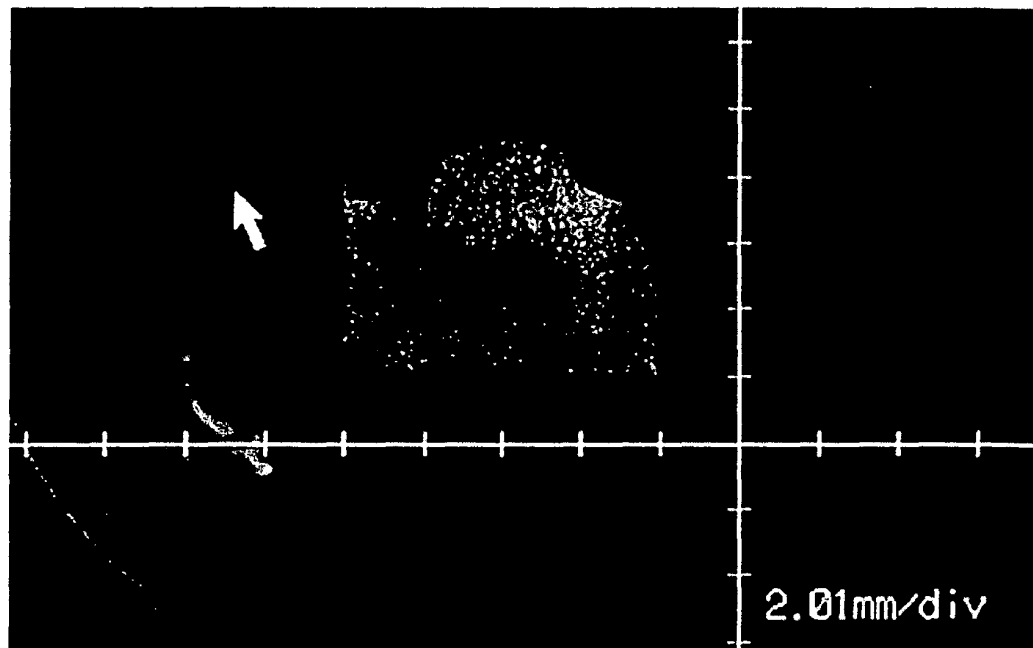


Fig.8

SHAPING EXAMPLE: TOP DIE EXTRUSION SPEED: 0.0003mm/sec
LOAD WEIGHT: 45kN (4.5tons)

CONVENTIONAL WROUGHT MATERIAL: AZ31



PRESENT ALLOY: Mg-0.6Al%Y

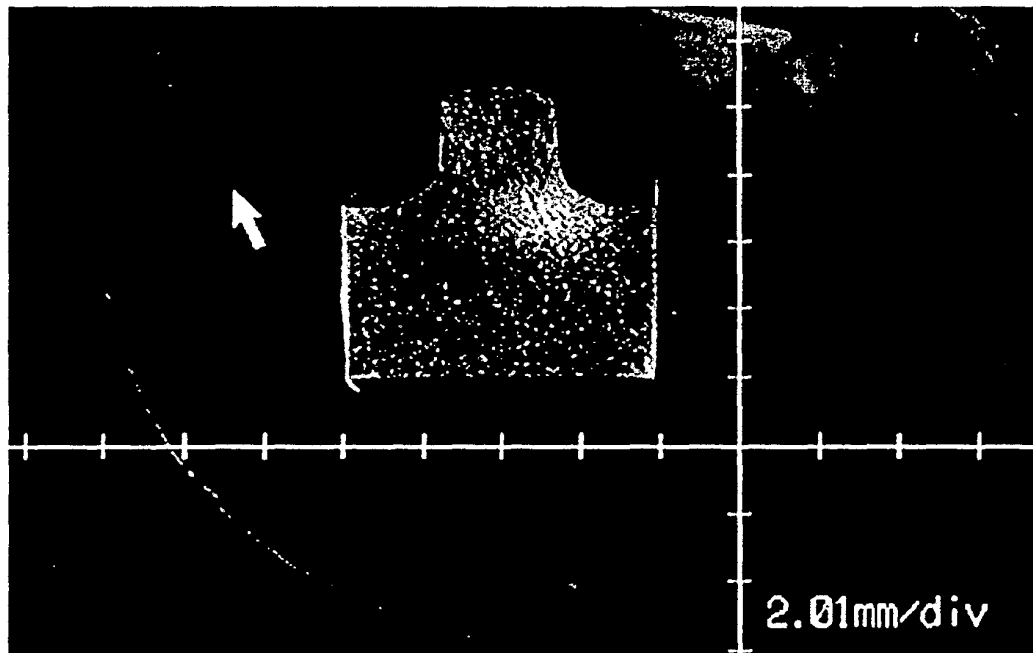
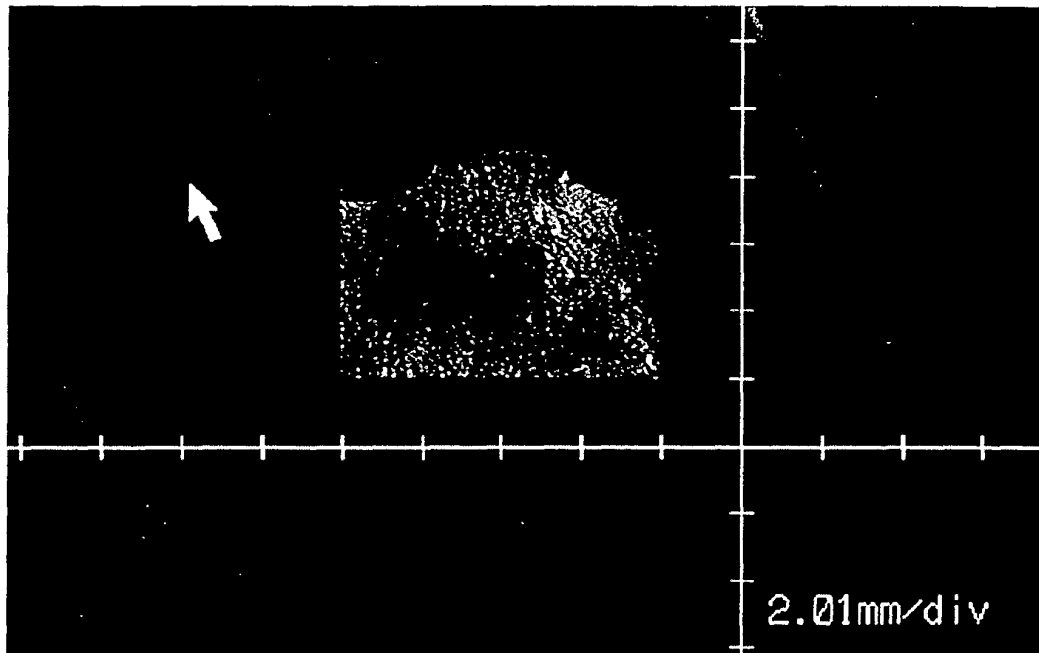


Fig.9

SHAPING EXAMPLE: TOP DIE EXTRUSION SPEED: 0.03mm/sec
LOAD WEIGHT: 45kN (4.5tons)

CONVENTIONAL WROUGHT MATERIAL: AZ31



PRESENT ALLOY: Mg-0.6AT%Y

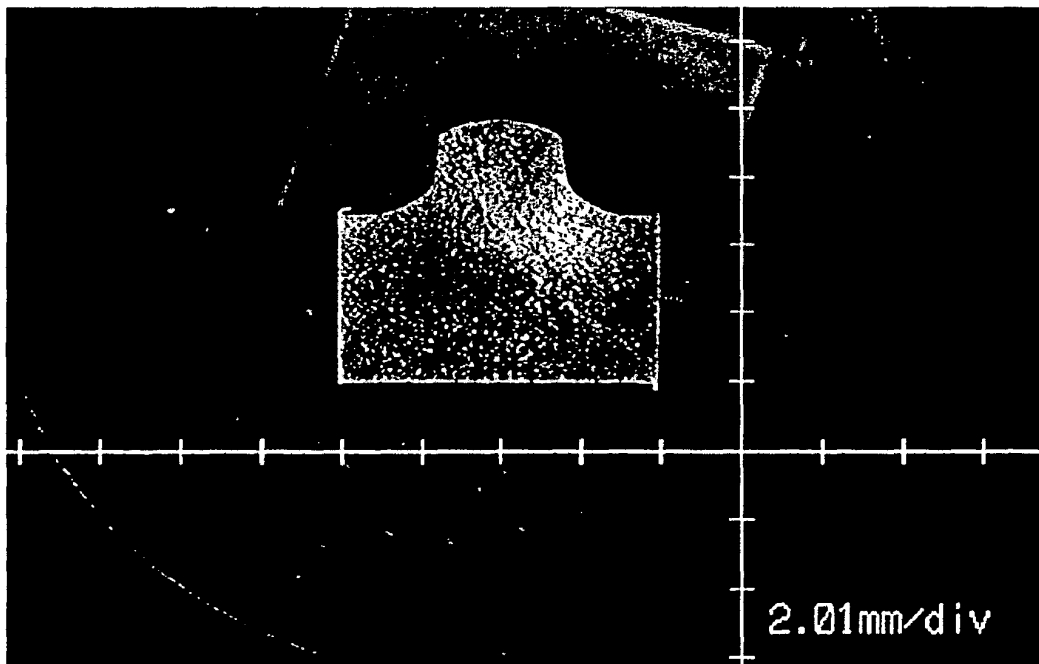


Fig.10

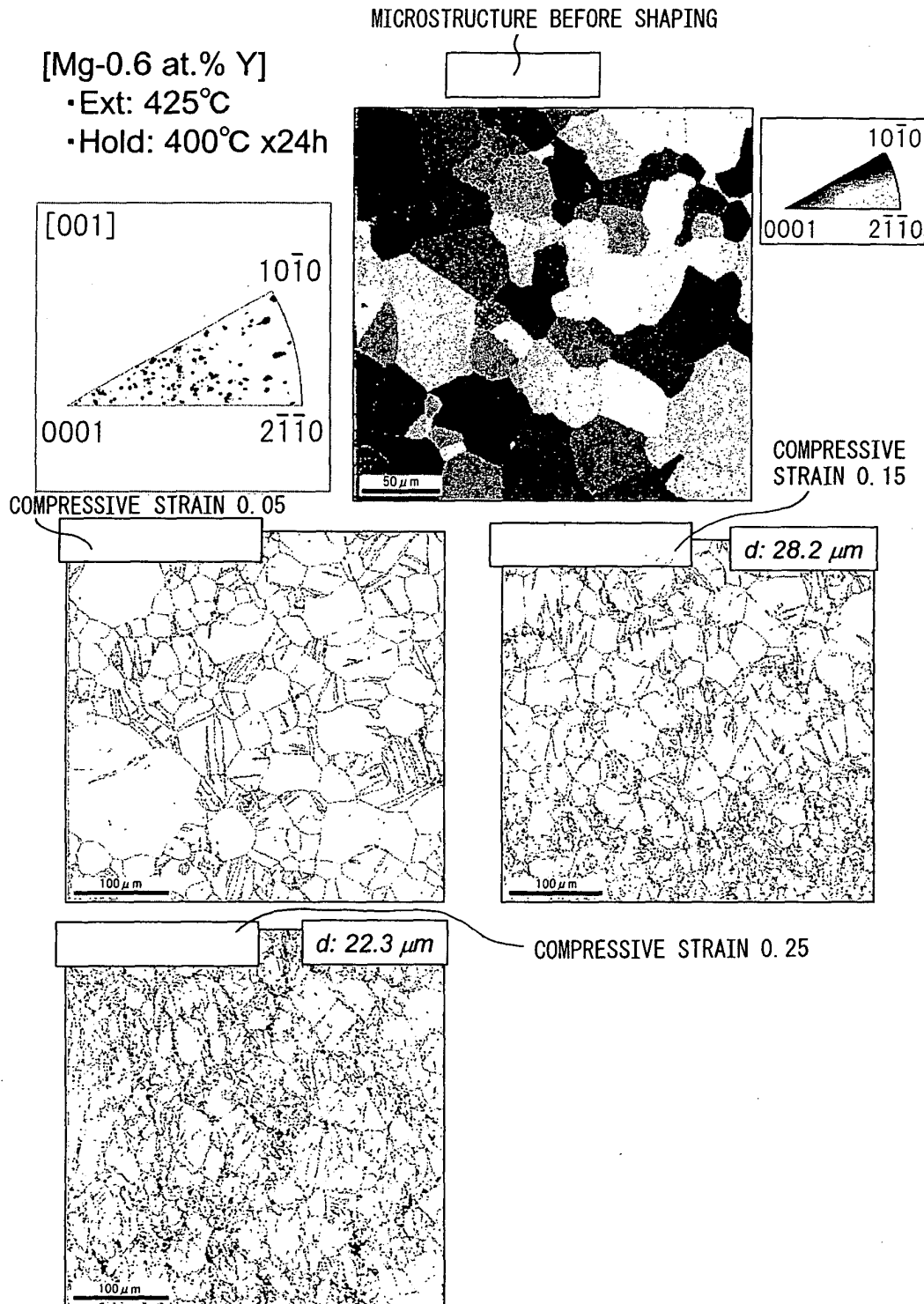


Fig.11

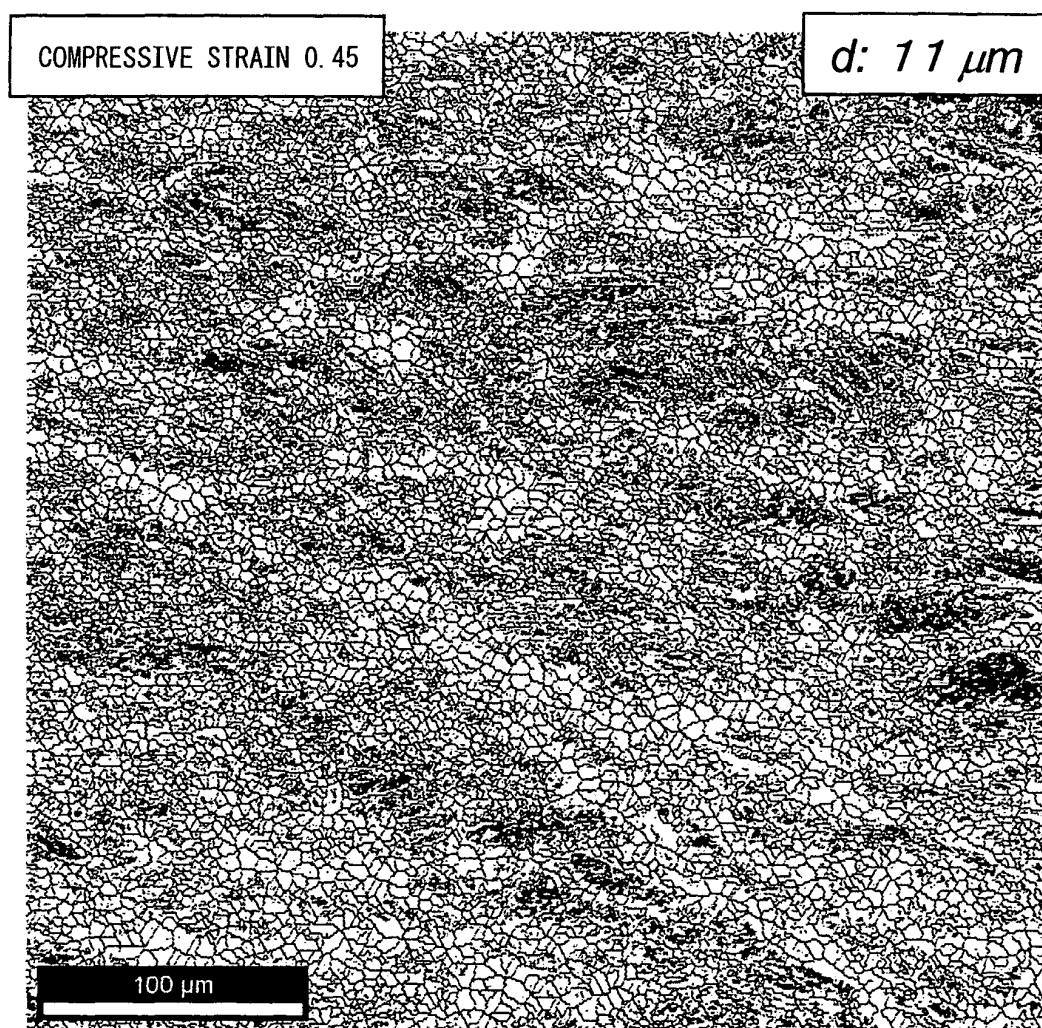


Fig.12

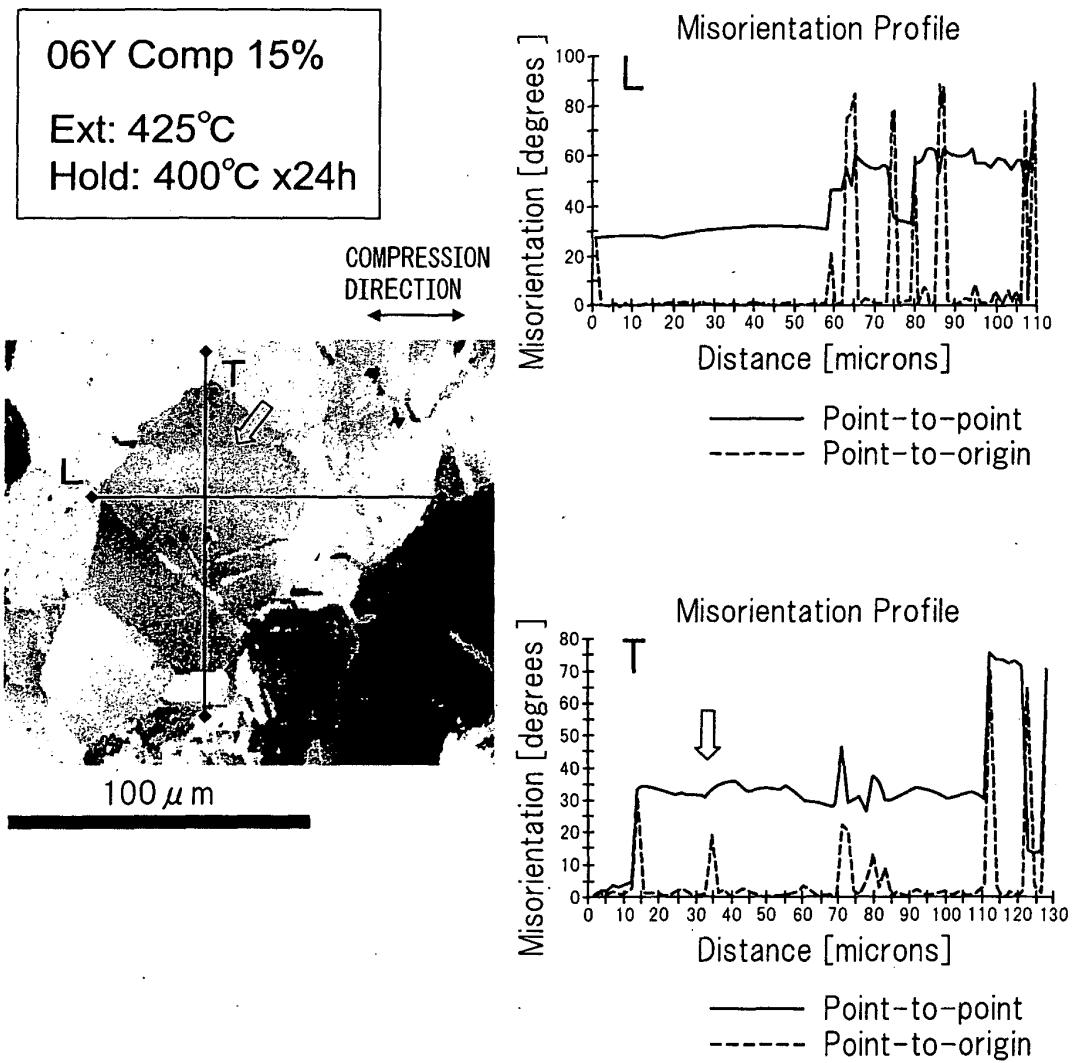


Fig.13

AZ31-250-400 - Forged @RT, 0.0003 mm/sec

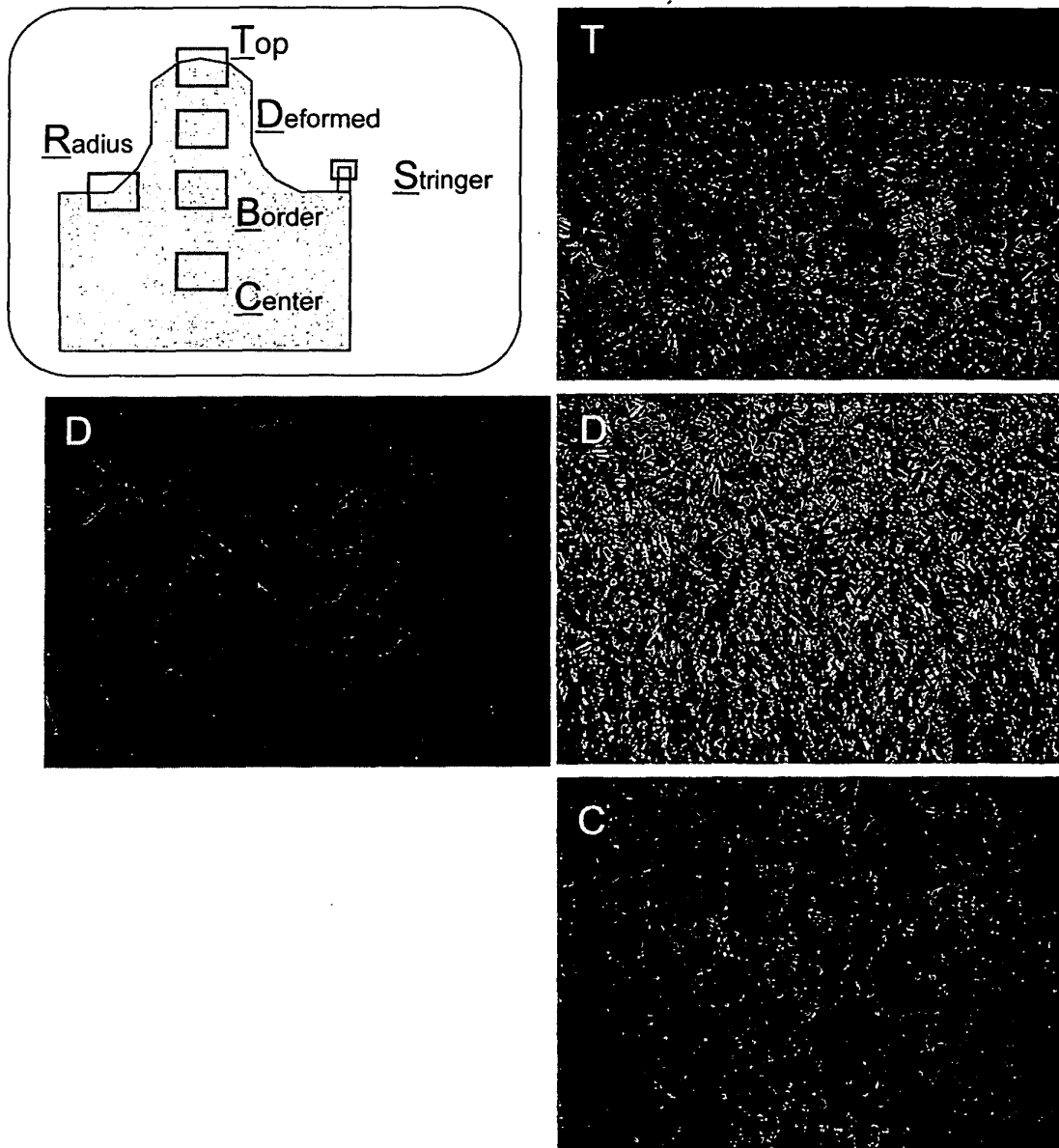


Fig.14

06Y-320-400

- Forged @RT, 0.0003 mm/sec
- EQUIVALENT PLASTIC STRAIN @D:-2.3

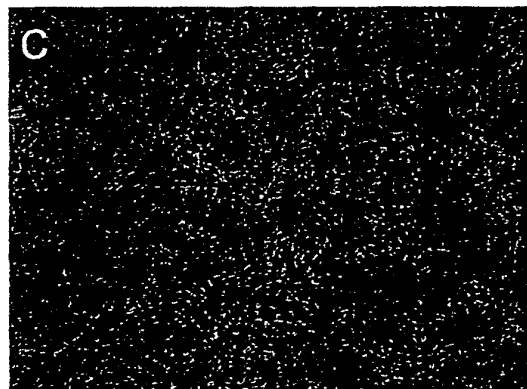
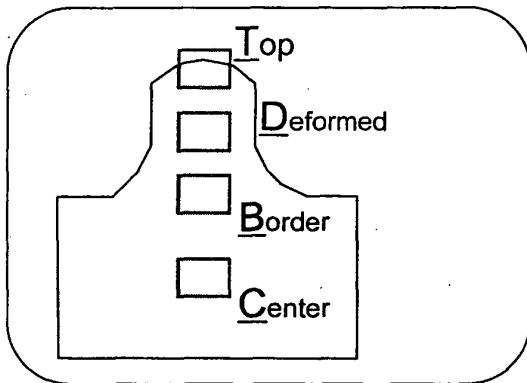


Fig.15

01Y-290-400

- Forged @RT, 0.0003 mm/sec
- EQUIVALENT PLASTIC STRAIN @D:-2.3

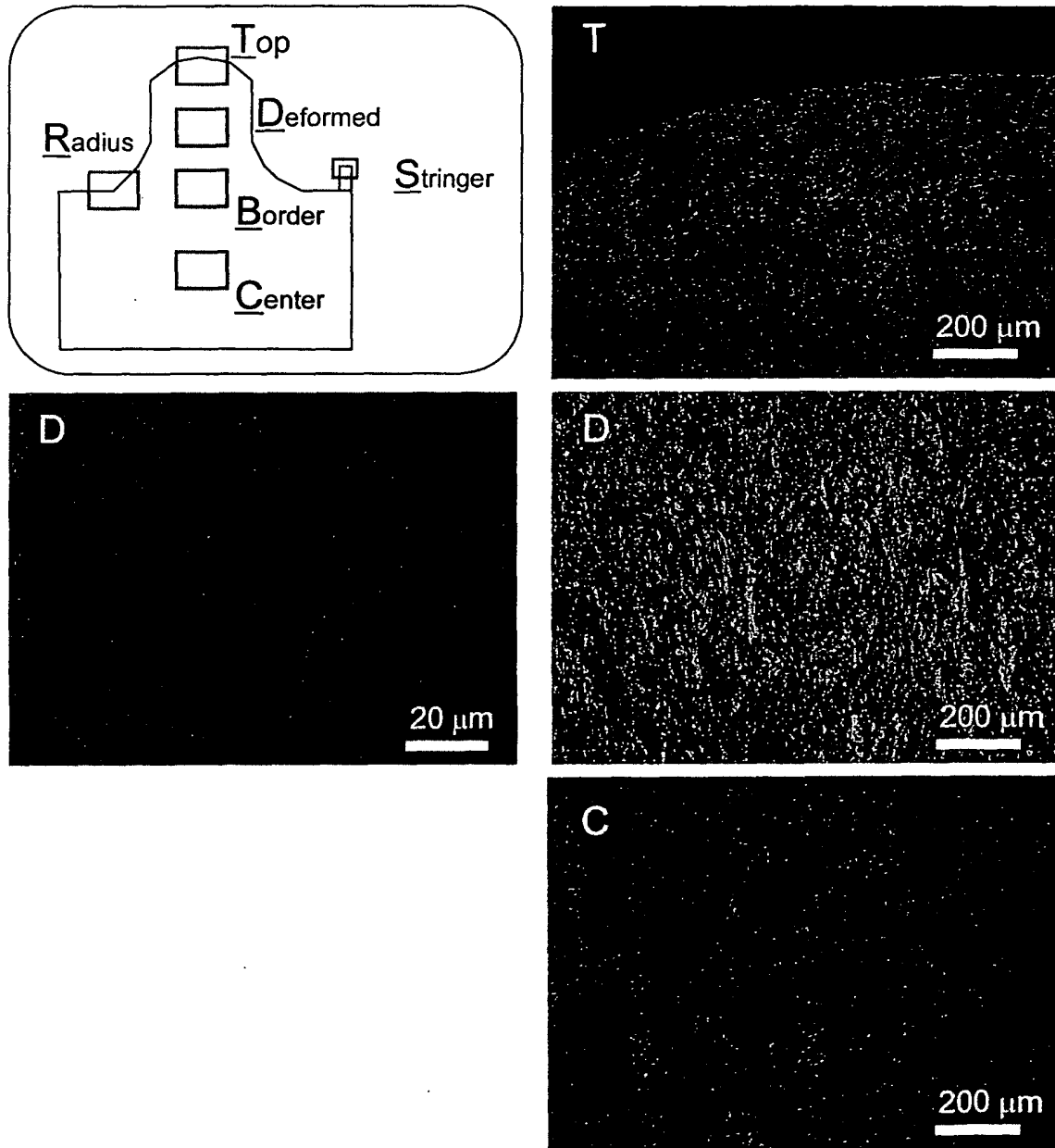


Fig.16

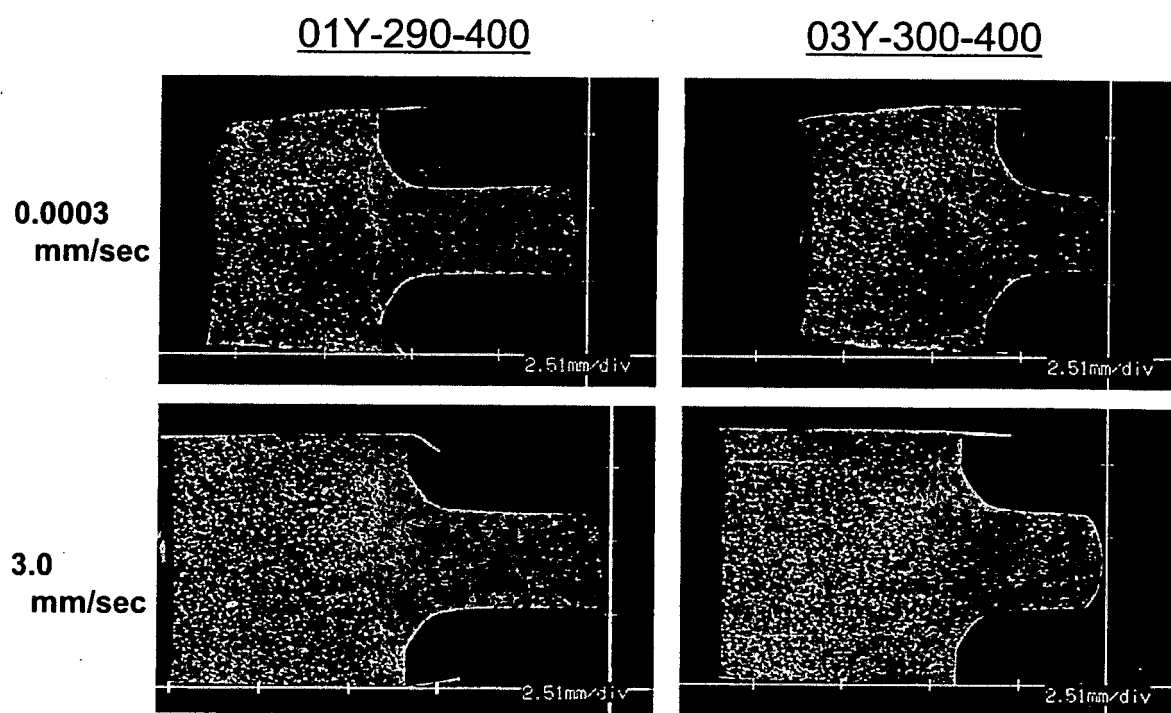


Fig.17

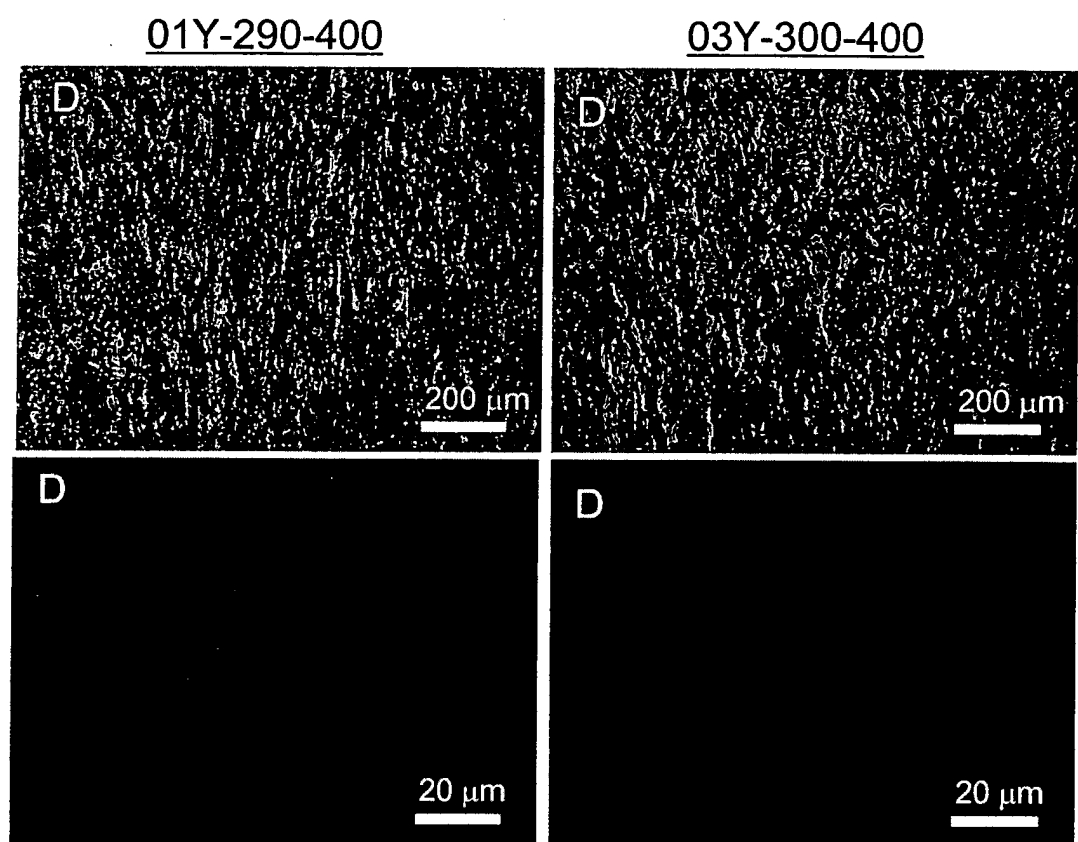
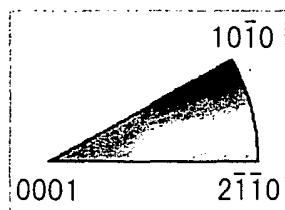
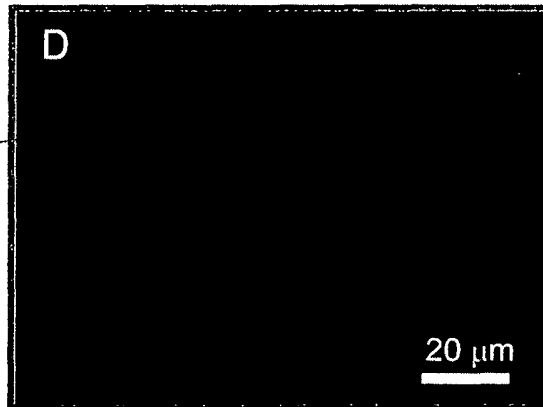
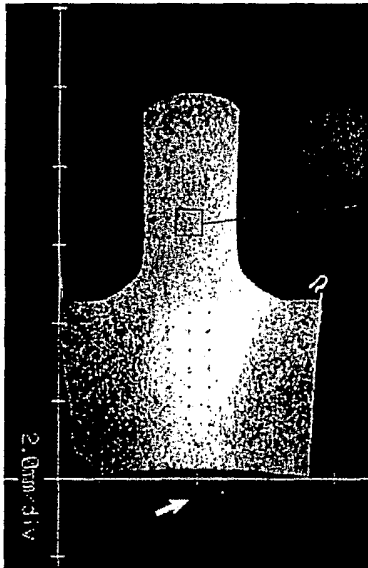


Fig.18

- Forged @RT, 0.0003 mm/sec
- EQUIVALENT PLASTIC STRAIN @D:-2.3



FROM RESULTS OF SEM/EBSD
OBSERVATION, BOUNDARIES
OBSERVED BY OPTICAL
MICROSCOPE ARE HIGH SLANT
ANGLE GRAIN BOUNDARIES

Fig.19

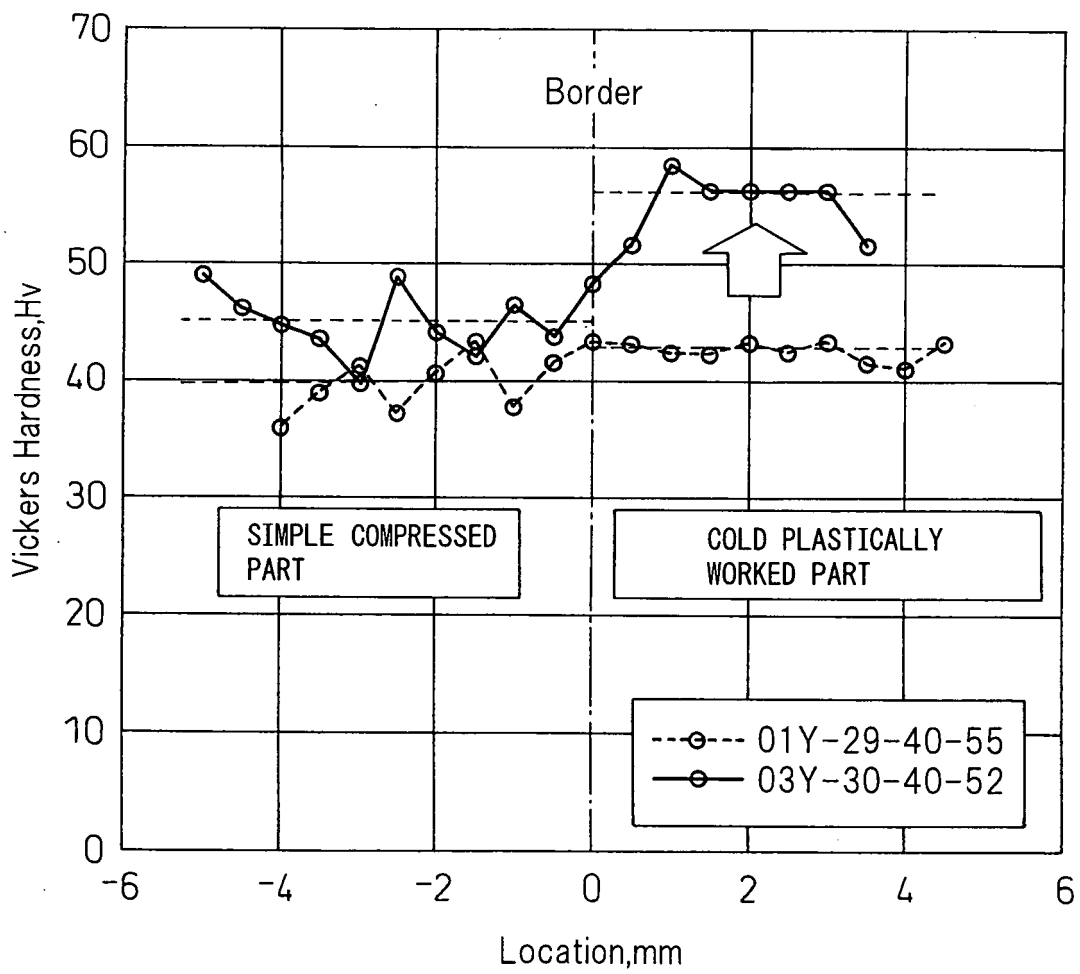


Fig.20

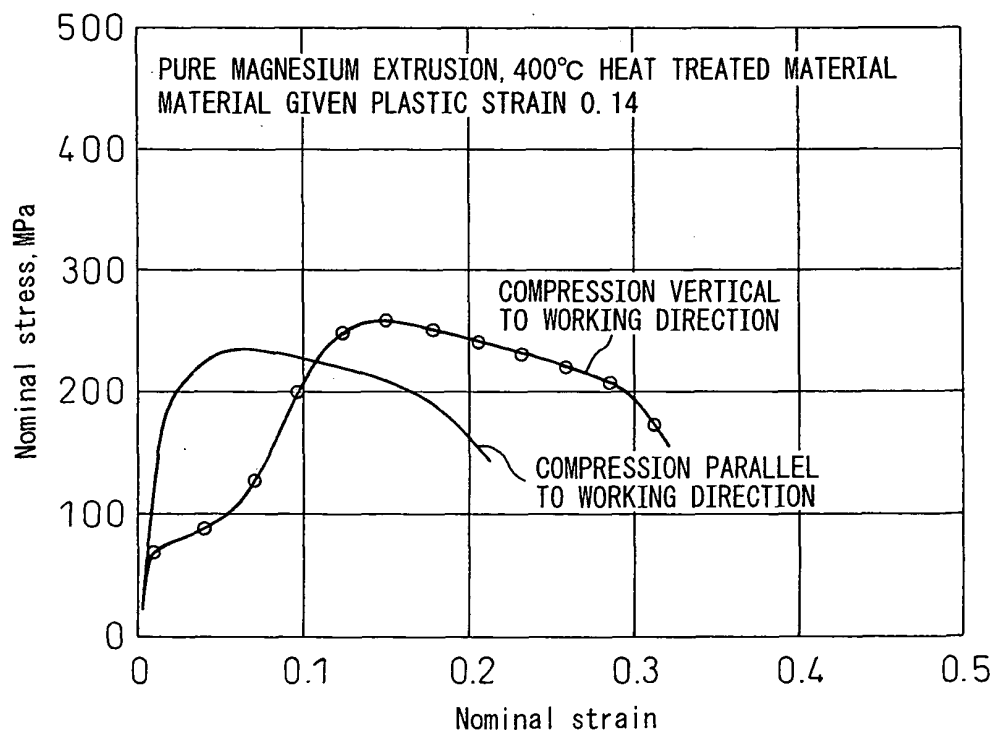
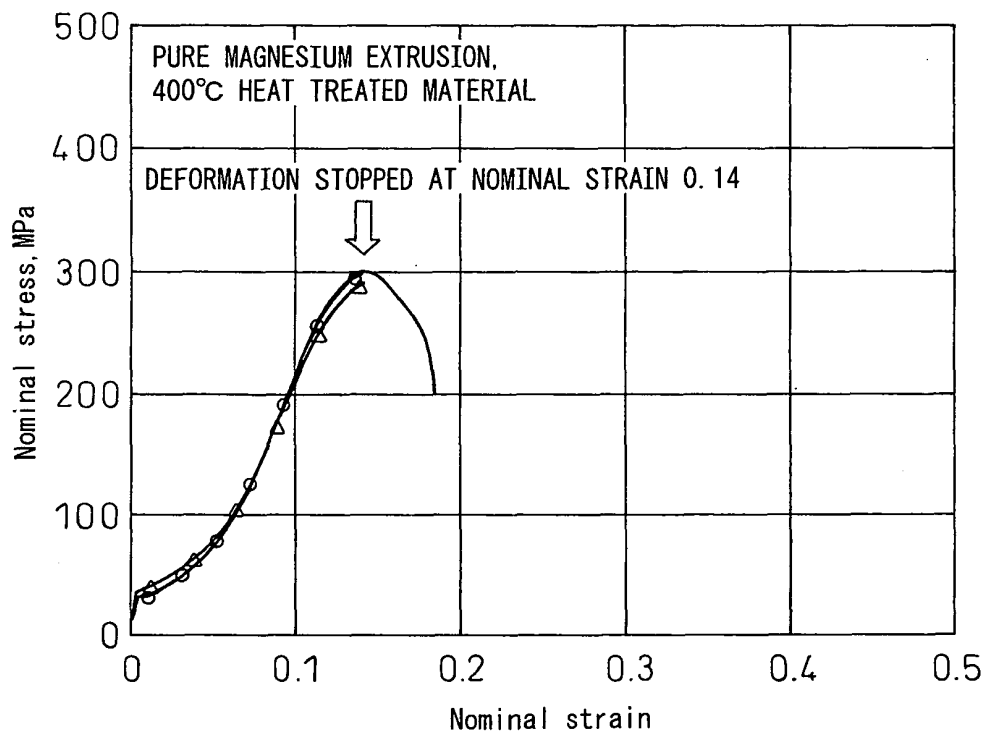


Fig.21

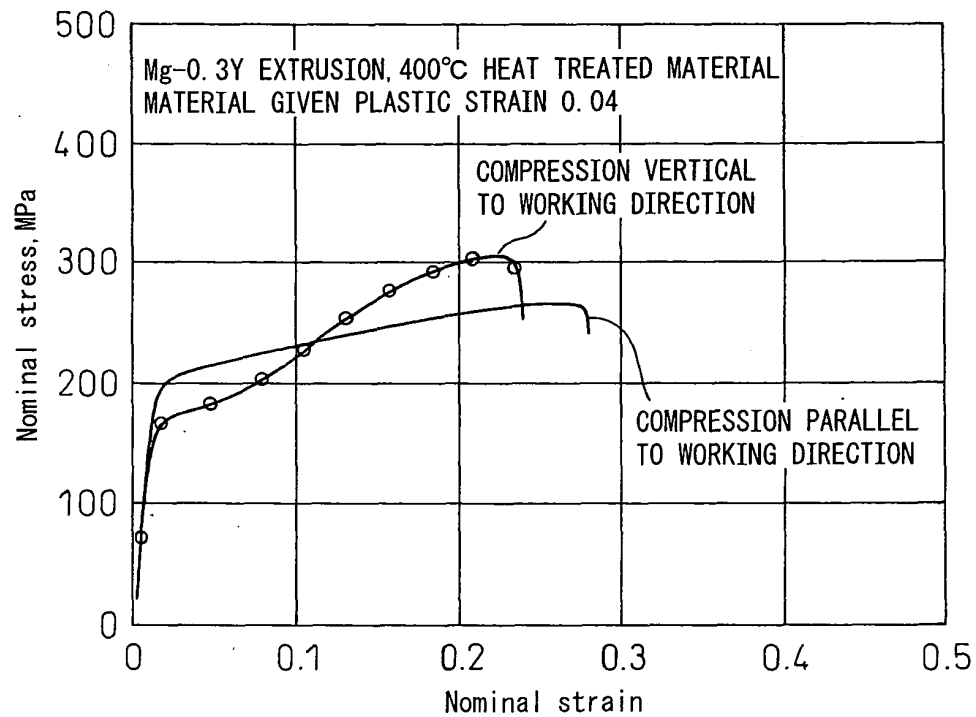
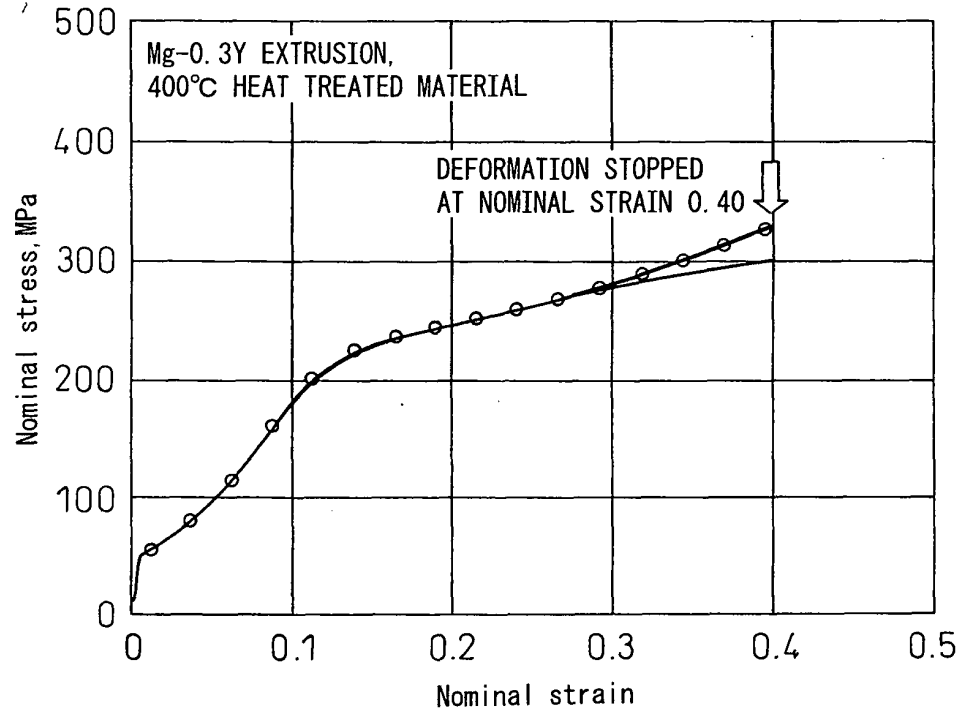


Fig.22

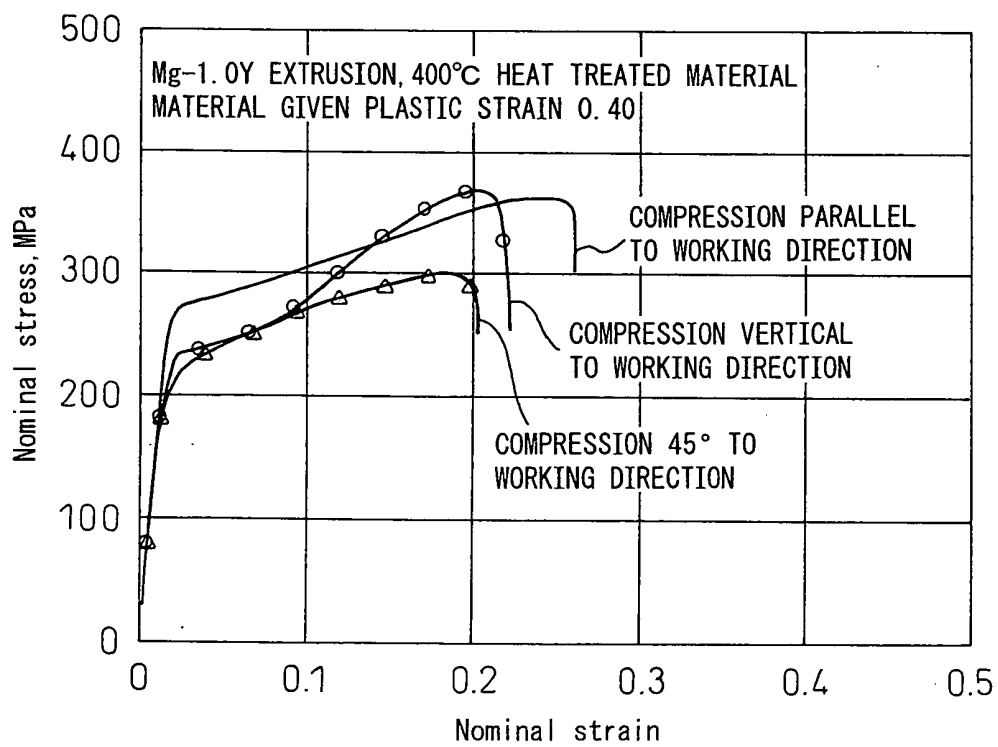
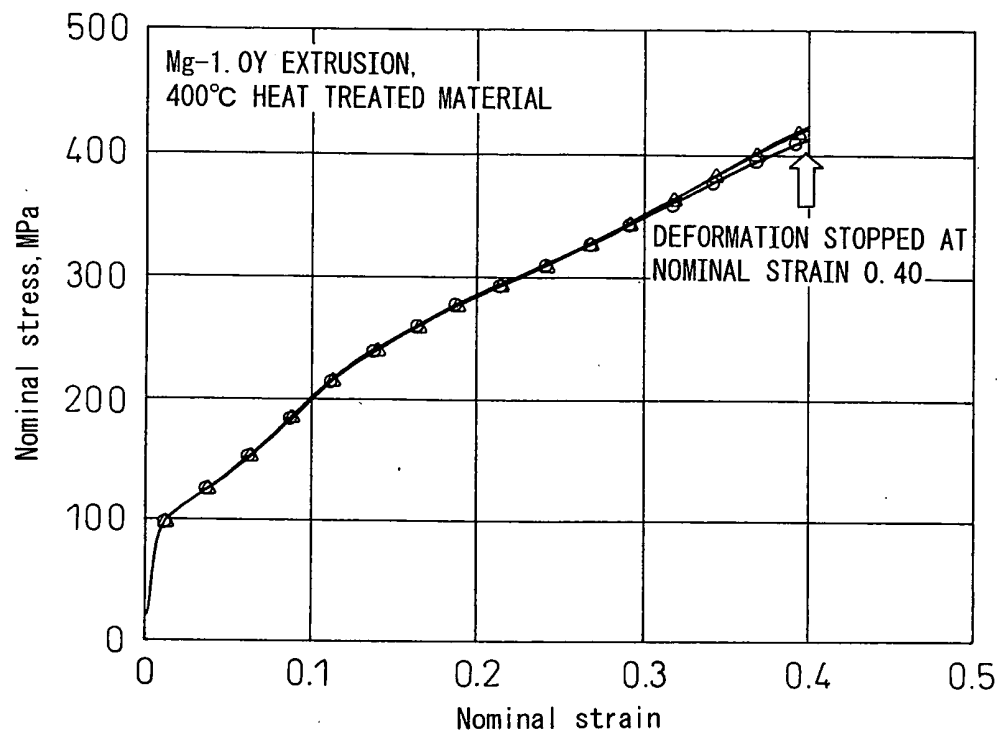


Fig.23

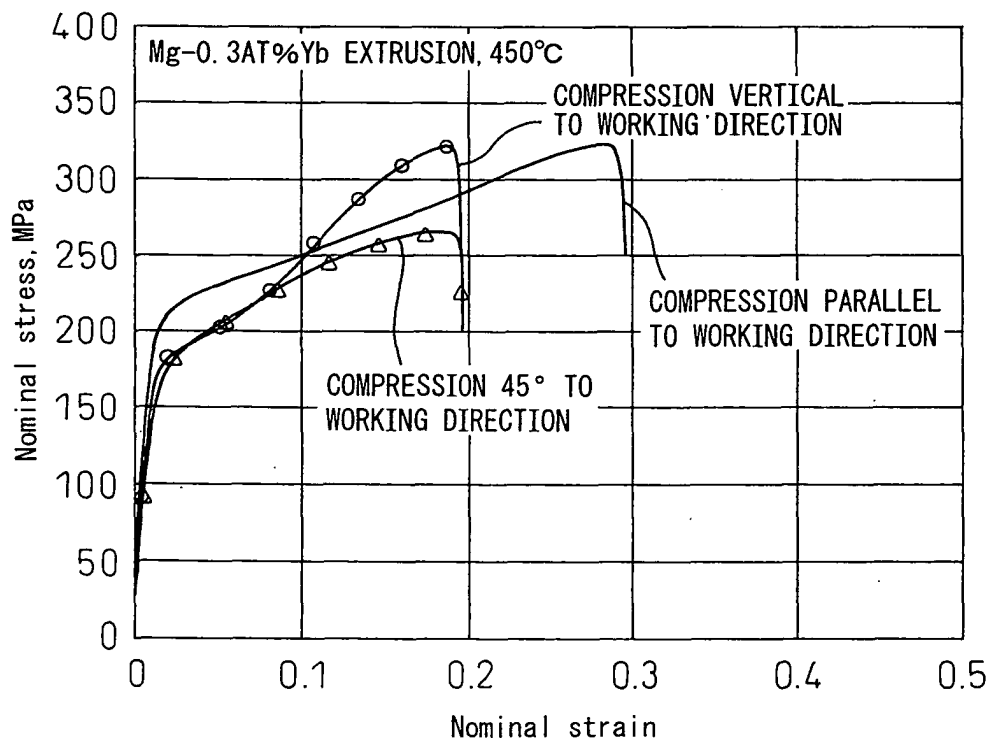
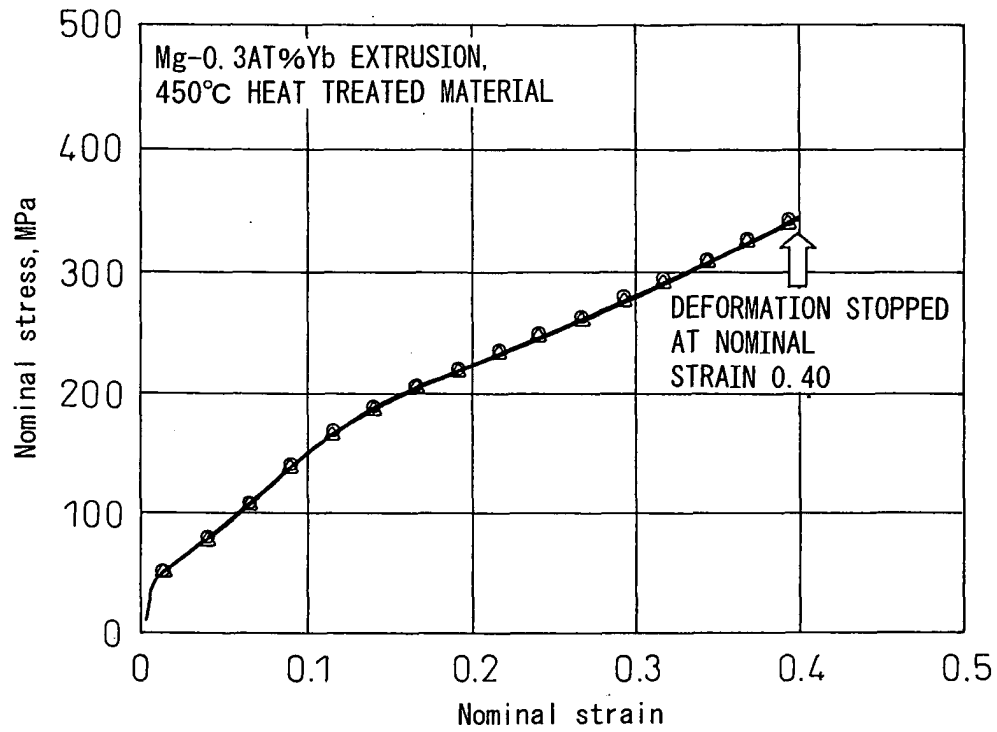


Fig.24

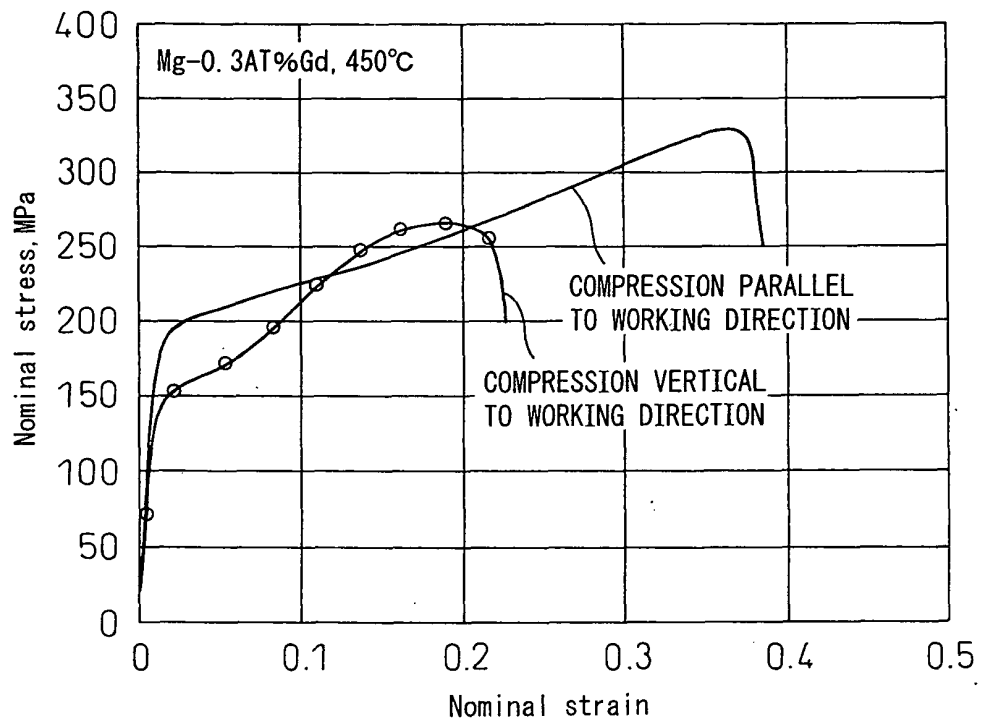
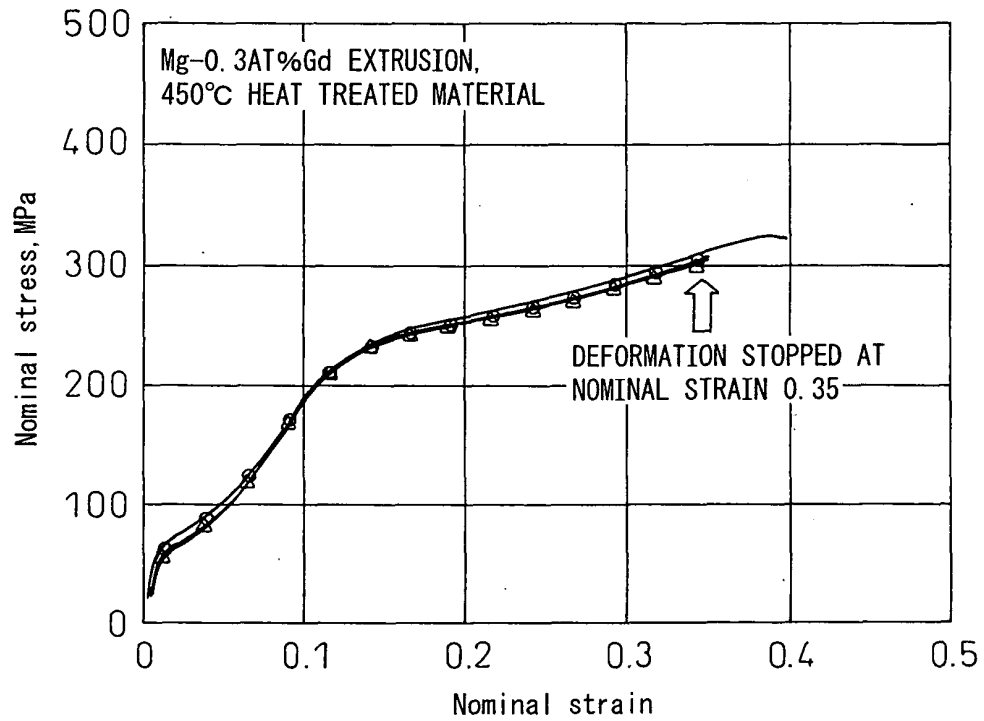


Fig.25

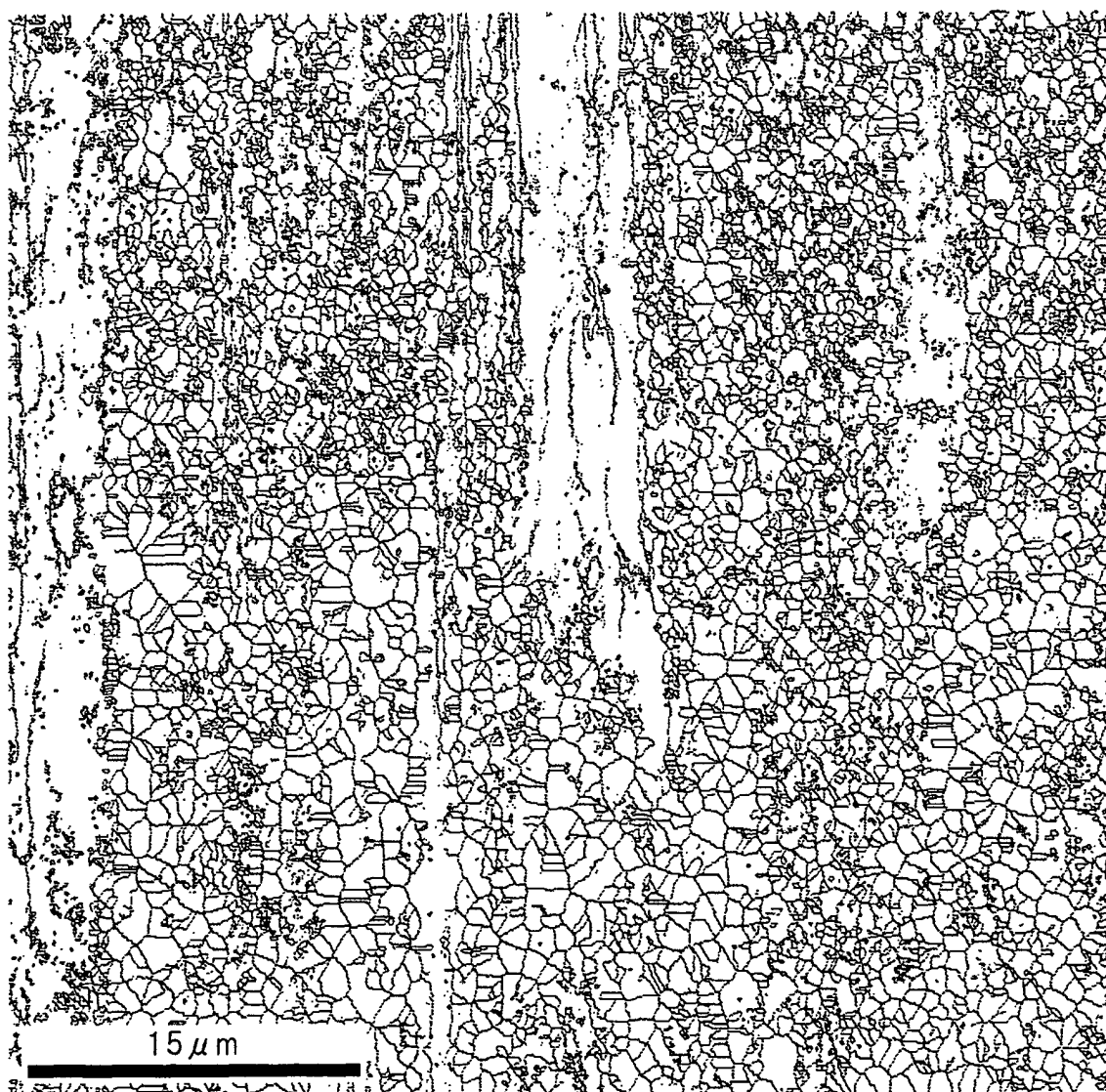
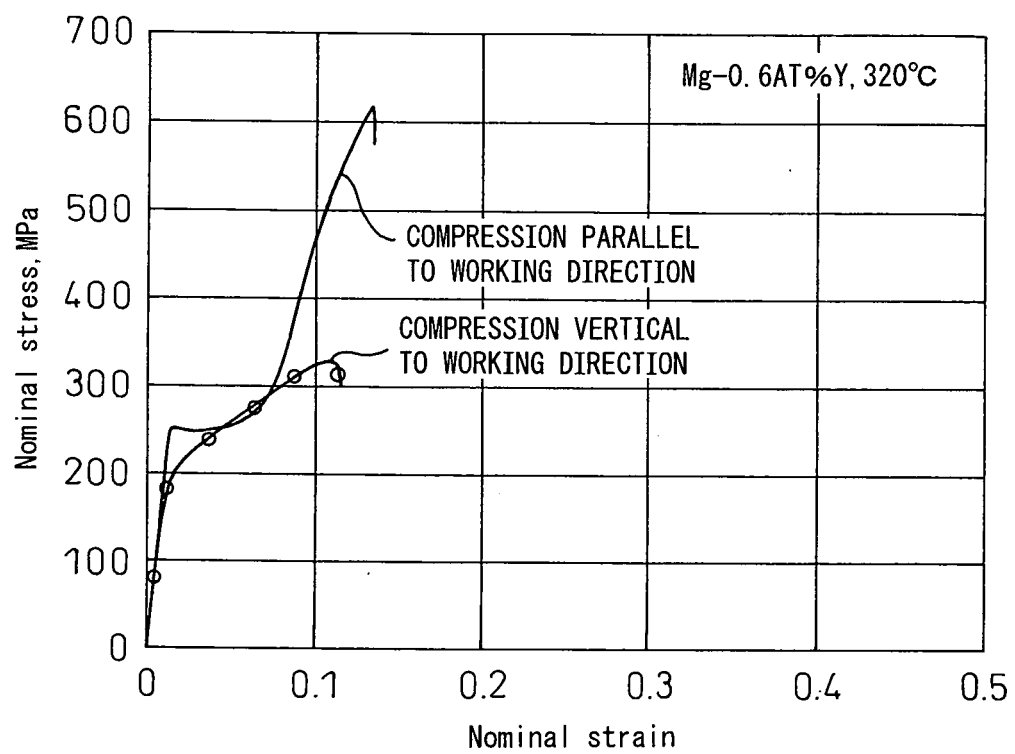


Fig.26



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2009/063452

A. CLASSIFICATION OF SUBJECT MATTER

C22C23/06(2006.01)i, C22F1/06(2006.01)i, C22F1/00(2006.01)n

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C23/00-23/06, C22F1/06, C22F1/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2009
Kokai Jitsuyo Shinan Koho	1971-2009	Toroku Jitsuyo Shinan Koho	1994-2009

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2001-294966 A (Matsushita Electric Industrial Co., Ltd.), 26 October 2001 (26.10.2001), claims 1, 5 to 6; paragraph [0026] (Family: none)	1-4
X	WO 2006/003899 A1 (Sumitomo Electric Industries, Ltd.), 12 January 2006 (12.01.2006), claims 10, 12, 32, 41, 44, 46; paragraph [0046] & US 2008/0311423 A1 & EP 001777022 A1 & CA 002572480 A & KR 10-2007-0030243 A & CN 001980759 A	1-4

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

* Special categories of cited documents:

"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 date

"L" 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)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" 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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search
08 October, 2009 (08.10.09)Date of mailing of the international search report
20 October, 2009 (20.10.09)Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2009/063452

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 09-041066 A (Mitsui Mining & Smelting Co., Ltd.), 10 February 1997 (10.02.1997), claims 2 to 4 (Family: none)	1-4
X	JP 2008-214668 A (National Institute of Advanced Industrial Science and Technology), 18 September 2008 (18.09.2008), claims 9, 12; paragraph [0040] (Family: none)	1-4
X	JP 2003-328065 A (Toyo Kohan Co., Ltd.), 19 November 2003 (19.11.2003), claim 1; paragraphs [0015], [0021], [0024] (Family: none)	1-4
X	WO 2007/058276 A1 (Independent Administrative Institution National Institute for Materials Science), 24 May 2007 (24.05.2007), claim 7; paragraph [0033] & US 2009/0171452 A1 & EP 001959025 A	1-4
X	JP 2006-016658 A (Independent Administrative Institution National Institute for Materials Science), 19 January 2006 (19.01.2006), claim 3 & US 2008/0017285 A1 & WO 2006/004072 A1 & KR 10-2007-0027642 A & CN 001981064 A	1-4

Form PCT/ISA/210 (continuation of second sheet) (April 2007)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2009/063452

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

The matters common to the inventions of claims 1-4 are matters set forth in claim 1. However, any matter specified in claim 1 is not novel as disclosed in JP 2001-294966 A (claim 1, claims 5-7, paragraph [0026]) and so on. Thus, there is no special technical feature common to the inventions of claims 1-4.

Further, the inventions of claims 3,4 are not novel as disclosed in JP 2001-294966 (claim 1, claims 5-7, paragraph [0026]) and so on, while the invention of claim 2 is also not novel as disclosed in JP 09-041066 A (claims 2-4) and so on.

(continued to extra sheet)

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest
the

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (2)) (April 2007)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2009/063452

Continuation of Box No.III of continuation of first sheet(2)

Consequently, the inventions of claims 1-4 have no common special technical feature and are therefore not considered to satisfy the requirement of unity of invention. Thus, the number of inventions of this application is considered to be 4, which is the same as the number of claims.