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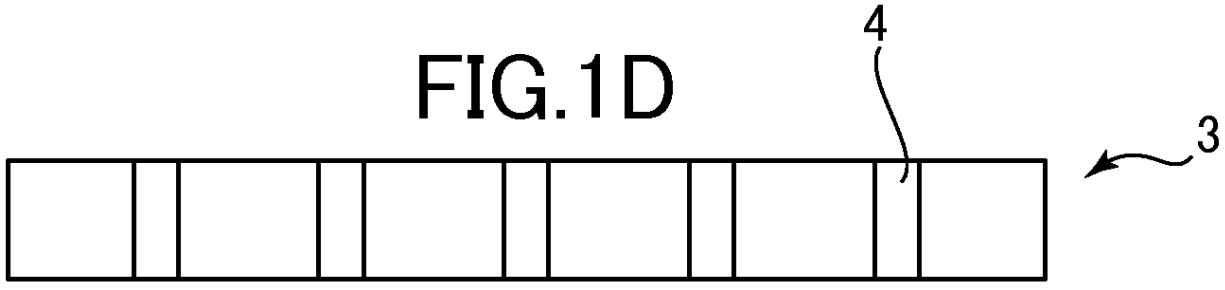
(54) **POROUS NICKEL THIN FILM AND MANUFACTURING METHOD THEREOF**

(57) Provided is a porous nickel thin film having a flexibility value of no more than 15.0 N/mm.

FIG.1D



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Description

Technical Field

[0001] The present invention relates to a porous nickel thin film and a manufacturing method thereof.

Background Art

[0002] Nickel thin films are expected to be applied to numerous fields. For example, Japanese Patent No. 4411409 (Patent Literature 1) describes that a porous nickel plated film is used as a support for a hydrogen permeable metal membrane. For this application, there is a case where flexibility is required in a nickel thin film.

Citation List

Patent Literature

[0003] Patent Literature 1: Japanese Patent No. 4411409

Summary of Invention

[0004] An object of the present invention is to provide a nickel thin film excellent in flexibility and a manufacturing method thereof.

[0005] The inventors have found that a porous nickel thin film obtained by using a particular method greatly surpasses in flexibility a nickel thin film obtained by using the conventional method.

[0006] To be more specific, the present invention includes the following aspects:

[1] A porous nickel thin film having a flexibility value of 15.0 N/mm or less, the flexibility value being a value measured by a method including the steps of:

supporting an entire periphery of the nickel thin film with a subject supporting jig so as to form an unsupported region with a closed shape in the nickel thin film;
measuring a relationship between a force applied to a pushing jig and a displacement amount of the pushing jig by pushing one end of the pushing jig against the unsupported region perpendicularly to the nickel thin film; and
obtaining a value (N/mm) by dividing the force (N) applied to the pushing jig by the displacement amount (mm) of the pushing jig, as the flexibility value.

[2] The porous nickel thin film according to [1] described above, having a thickness of 0.1 to 100 μm.

[3] A method for manufacturing a porous nickel thin film, including the steps of:

forming a nickel plated film on a conductive substrate by use of a nickel electroplating bath containing a nickel salt and a surfactant; and
heat-treating the nickel plated film so as to burn and remove the surfactant taken in the nickel plated film.

[4] The method according to [3] described above, in which the porous nickel thin film has a flexibility value of 15.0 N/mm or less, and the flexibility value is a value measured by a method including the steps of:

supporting an entire periphery of the nickel thin film with a subject supporting jig so as to form an unsupported region with a closed shape in the nickel thin film;
measuring a relationship between a force applied to a pushing jig and a displacement amount of the pushing jig by pushing one end of the pushing jig against the unsupported region perpendicularly to the nickel thin film; and
obtaining a value (N/mm) by dividing the force (N) applied to the pushing jig by the displacement amount (mm) of the pushing jig, as the flexibility value.

[5] The method according to [3] or [4] described above, in which
the surfactant contains an anionic surfactant.

[6] The method according to [5] described above, in which
the anionic surfactant contains a compound selected from the group consisting of a polyoxyalkylene alkyl ether sulfate, a polyoxyalkylene alkyl ether carboxylate, and an alkylbenzene sulfonate.

[7] The method according to any one of [3] to [6] described above, in which
the step of forming a nickel plated film includes a step of carrying out pulse electroplating.
[8] The method according to any one of [3] to [7], in which the conductive substrate is a Ti substrate, a Cu substrate, an SUS substrate, a glass given electrical conductivity, or a resin given electrical conductivity.
[9] The method according to any one of [3] to [8] described above, further including a step of peeling the porous nickel thin film off the conductive substrate.

[0007] The present invention provides a nickel thin film excellent in flexibility and a manufacturing method thereof.

Brief Description of Drawings

[0008]

Fig. 1A is a cross-sectional view schematically showing a method of manufacturing a porous nickel thin film.
Fig. 1B is a cross-sectional view schematically showing the method of manufacturing the porous nickel thin film.
Fig. 1C is a cross-sectional view schematically showing the method of manufacturing the porous nickel thin film.
Fig. 1D is a cross-sectional view schematically showing the method of manufacturing the porous nickel thin film.
Fig. 2 is a view of an external appearance showing an evaluation apparatus.
Fig. 3 is a schematic view showing the evaluation apparatus.
Fig. 4 is a cross-sectional view schematically showing a pair of clamping members.
Fig. 5 is a schematic view showing an example of a pushing jig.
Fig. 6 is a schematic view showing a method of evaluating flexibility.
Fig. 7 is a graph showing results of measuring flexibility.
Fig. 8 is a graph showing results of calculating flexibility values.

Description of Embodiment

[0009] Hereinafter, an embodiment of the present invention is described.

(Method of Manufacturing Porous Nickel Thin Film)

[0010] Fig. 1A to Fig. 1D are cross-sectional views schematically showing a method of manufacturing a porous nickel thin film according to the embodiment.
[0011] First, as shown in Fig. 1A, a conductive substrate 1 is prepared.
[0012] Next, as shown in Fig. 1B, a nickel plated film 2 is formed on the conductive substrate 1.
[0013] The nickel plated film 2 is formed using a nickel electroplating bath which contains a nickel salt and a surfactant. Since the nickel electroplating bath contains a surfactant here, the nickel plated film 2 formed has the surfactant taken therein.
[0014] Next, as shown in Fig. 1C, the nickel plated film 2 is heat-treated. Heat treatment burns and removes the surfactant taken in the nickel plated film 2. Then, pores 4 penetrating in the thickness direction are formed in the nickel plated film 2, and a porous nickel thin film 3 is obtained as a result.
[0015] In the case of using the nickel thin film 3 as a single-layered film, the nickel thin film 3 is peeled off the conductive substrate 1 as shown in Fig. 1D. In this case, to peel off the nickel thin film 3, it suffices to use in advance a substrate with low adhesion to the nickel thin film 3 as the conductive substrate 1. Such a substrate includes a metal substrate such as for example a Ti substrate, a Cu substrate, and an SUS substrate, and glass and resin material which are given electrical conductivity. Note that heat treatment for removing the surfactant may be carried out after the nickel thin film 3 is peeled off the conductive substrate 1.
[0016] On the other hand, the nickel thin film 3 does not necessarily have to be peeled off the conductive substrate 1. Depending on the intended use, one may use a stack of the conductive substrate 1 and the nickel thin film 3 for the end use without peeling the nickel thin film 3 off the conductive substrate 1.
[0017] By use of the manufacturing method described above, it is possible to obtain the porous nickel thin film 3 which is excellent in flexibility. To be more specific, by use of the manufacturing method described above, it is possible to obtain the porous nickel thin film 3 which has a flexibility value of 15.0 N/mm or less, preferably 10.0 N/mm or less, more preferably 1.0 to 10.0 N/mm, and still more preferably 3.0 to 8.0 N/mm. The porous nickel thin film 3 having such flexibility values is a novel metal film obtainable by the manufacturing method of the present invention, excellent in flexibility, and useful in various applications.
[0018] Note that the "flexibility value" in the present specification can be determined by the method of evaluating the porous nickel thin film and the method explained in Examples to be described later.

[0019] In addition, the porous nickel thin film 3 obtained in the embodiment is also excellent in thermal resistance. There is a case where the shape of a nickel thin film manufactured by e.g. rolling is not maintained because oxidation proceeds during high temperature heating. In contrast, the shape of the porous nickel thin film 3 obtained in the embodiment is maintained even during high temperature heating.

[0020] The thickness of the nickel thin film 3 obtained in the embodiment is preferably 0.1 μm to 100 μm, more preferably 1 μm to 10 μm, and still more preferably 2 μm to 8 μm. Too large a thickness makes it difficult to form pores, raises the processing difficulty, and leads to an increase in the manufacturing cost. Conversely, too small a thickness leads to insufficient strength.

[0021] The use of the nickel thin film 3 obtained in the embodiment is not particularly limited. For example, the nickel thin film 3 is useful as: a high performance catalytic film; a high performance filter; an undercoat for coating, painting, and plating; a functional coat and a thermal radiation coat used at high temperatures; and a surface coat for a slidable component.

[0022] In the case of use as a high performance catalytic film, the nickel thin film 3 is used as-is, or catalytic particles such as Pt and Pd particles are scattered and held in the pores of the nickel thin film 3. In the case of use as a high performance filter, the penetration pores formed in the nickel thin film 3 are used as fluid passages. In the case of e.g. a high performance catalytic film and a high performance filter, flexibility is important in terms of the life of the coat. The nickel thin film 3 of the embodiment is preferable because it can satisfy such a requirement.

[0023] In addition, the nickel thin film 3 obtained in the embodiment is useful as a functional coat and a thermal radiation coat which are required to have thermal resistance because it is not broken even under a high temperature atmosphere.

[0024] Moreover, the nickel thin film 3 of the embodiment has a large surface area because it is provided with pores. For this reason, if the nickel thin film 3 is used as an undercoat for e.g. coating, painting, and plating, it is possible to increase physical adhesion between the nickel thin film 3 and a film formed thereon.

[0025] Furthermore, if the nickel thin film 3 of the embodiment is used as a surface coat of a slidable component, it is possible to enhance lubricant retainability and to extend the life of the slidable component thanks to the pores provided.

(Plating Bath and Plating Conditions)

[0026] Subsequently, detailed descriptions are provided for a nickel electroplating bath used in the embodiment and the plating conditions. As in the foregoing description, the plating bath used in the embodiment is an aqueous solution containing a nickel salt and a surfactant.

[0027] The nickel salt acts as a supply source of nickel ions. Although the nickel salt is not particularly limited, it is preferable to use a compound selected from the group consisting of nickel sulfamate, nickel chloride, nickel sulfate, and nickel citrate. Among these, the nickel salt preferably contains nickel sulfamate. A coating with a low internal stress and high flexibility is obtained by use of nickel sulfamate.

[0028] The concentration of the nickel salt in the plating bath is preferably 100 g/L to 800 g/L. Too high a concentration of the nickel salt reduces the saturation concentration of the surfactant, makes it difficult to form pores, and increases the possibility of losing flexibility. Too low a concentration of the nickel salt reduces the limiting current density due to insufficient concentration of the metal salt, increases the possibility of producing hydrogen gas during the formation of the coating, and increases the risk of cracks caused by the occlusion of hydrogen into the conductive substrate 1 being the undercoat. Moreover, too low a concentration is likely to produce a rough Ni plated coating with numerous pinholes.

[0029] It is preferable to use an ionic surfactant as the surfactant contained in the plating bath. It is preferable to use an anionic surfactant as the ionic surfactant.

[0030] Preferable examples of the anionic surfactant include a compound selected from the group consisting of a polyoxyalkylene alkyl ether sulfate, a polyoxyalkylene alkyl ether carboxylate, a polyoxyalkylene alkyl ether sulfosuccinate, a polyoxyalkylene alkyl ether phosphate, a polyoxyalkylene alkyl ether acetate, an alkylbenzene sulfonate, a higher alcohol sulfate, a polyoxyalkylene styrenated phenyl ether sulfate, an alkyl diphenyl ether sulfonate, an alpha olefin sulfonate, a dialkyl sulfosuccinate, an alkane sulfonate, a secondary alkane sulfonate, an alkyl naphthalene sulfonate, a formaldehyde condensate of a naphthalene sulfonate, a higher alcohol phosphate ester, a polyoxyalkylene styrenated phenyl ether phosphate, fatty acid soap, disproportionated rosin soap, and turkey red oil. A more preferable compound is one selected from the group consisting of the polyoxyalkylene alkyl ether sulfate, the polyoxyalkylene alkyl ether carboxylate, the polyoxyalkylene alkyl ether acetate, and the alkylbenzene sulfonate among the above.

[0031] Note that each of the polyoxyalkylene alkyl ether sulfate and the polyoxyalkylene alkyl ether carboxylate is preferably an ethylene oxide-containing compound expressed by Formula 1 below:

(Formula 1) : $R1\text{-}O\text{-}(CH_2CH_2O)_n\text{-}X$

[0032] Note that in Formula 1, R1 represents an alkyl group, preferably an alkyl group having 10 to 16 carbon atoms, and more preferably an alkyl group having 12 to 14 carbon atoms. The letter X indicates a sulfate or a carboxylate. The

letter n ranges from 1 to 20, preferably from 2 to 12.

[0033] In addition, the alkylbenzene sulfonate is preferably a compound having 8 to 16 carbon atoms in the alkyl group, more preferably a dodecylbenzene sulfonate.

[0034] The counter ions used as the salt of the anionic surfactant include alkali metal salts such as a sodium salt and a potassium salt, alkali earth metal salts, ammonium salts, and alkanolamine salts. Among these, the alkali metal salts are preferable, and the sodium salt is more preferable.

[0035] The concentration of the surfactant in the plating bath is preferably 0.1 mL/L to 100 mL/L, more preferably 1 mL/L to 50 mL/L, and still more preferably 5 mL/L to 30 mL/L. Too high a concentration of the surfactant makes it difficult to obtain a fine coating because plate deposition is hindered. On the other hand, too low a concentration makes it difficult to form pores, which makes it hard to obtain desired flexibility.

[0036] Other additives may be added to the plating bath such as a pH adjuster, a pH buffer, and a stress releaser. Sulfuric acid, sulfamic acid, nickel hydroxide, etc. are used as the pH adjuster, for example. Saccharin etc. are used as the stress releaser, for example.

[0037] The pH of the plating bath is preferably 2.0 to 4.5. Too high a pH reduces the limiting current density, increases the possibility of producing hydrogen gas, and increases the risk of occlusion of hydrogen into the conductive substrate 1. Moreover, the Ni coating is likely to become hard and brittle. On the other hand, too low a pH is likely to promote decomposition of the plating bath components.

[0038] The bath temperature of the plating bath during plating is preferably 40°C to 65°C. Too high a bath temperature is likely to promote the decomposition of the bath components. On the other hand, too low a bath temperature increases the possibility of surfactant precipitation. Moreover, extraneous deposition of nickel is likely to take place.

[0039] Although electroplating is possible using a direct current electrolysis, it is more preferable to carry out pulse electroplating. In the case of using pulse electroplating, at the early stages of deposition, it is possible to cause the surfactant to scatter and be adsorbed to the conductive substrate 1 being the undercoat, and to promote eutectoid between the surfactant and nickel during plating.

[0040] In the case of using pulse electroplating, the average current density is preferably 1 A/dm^2 to 20 A/dm^2. Too high an average current density may lead to excessive production of hydrogen, affecting the conductive substrate 1 being the undercoat. Furthermore, extraneous deposition of nickel might take place. On the other hand, too low an average current density makes it difficult to form pores, which makes it hard to obtain desired flexibility. Also, productivity is reduced.

[0041] The pulse current density is preferably 2 A/dm^2 to 20 A/dm^2. Too high a pulse current density may cause excessive production of hydrogen, affecting the conductive substrate 1 being the undercoat. Furthermore, extraneous deposition of nickel might take place. On the other hand, too low a pulse current density makes it difficult to form pores, reducing productivity.

[0042] The ratio of the pulse applying time ton to the pulse pause time toff (ton/toff) is more preferably 0.1 to 10. Too large a ratio (ton/toff) makes it difficult to form pores, which makes it hard to obtain desired flexibility. Conversely, too small a ratio also makes it difficult to form pores, which makes it hard to obtain desired flexibility.

[0043] The pulse frequency is preferably 0.1 to 1000 (Hz) . Too large a pulse frequency makes it difficult to form pores, which makes it hard to obtain desired flexibility. Conversely, too small a pulse frequency also makes it difficult to form pores, which makes it hard to obtain desired flexibility.

(Heat Treatment Conditions)

[0044] Subsequently, descriptions are provided for heat treatment conditions for burning and removing the surfactant. Heat treatment is carried out under the conditions where the surfactant is burnt and removed in, for example, the atmosphere, a reducing atmosphere such as hydrogen, or an inactive atmosphere such as nitrogen or argon.

[0045] To be more specific, the heat treatment temperature is 350°C to 900°C, for example. Besides, the heating time is 10 minutes to 120 minutes, for example. Too high a heating temperature is likely to increase the cost of mass production processing. Worse, the possibility of losing flexibility is increased because an interdiffusion layer is likely to be formed between the conductive substrate 1 being the undercoat and the nickel plated film 2. On the other hand, too low a heat treatment temperature makes it difficult for porosification to occur, which makes it impossible to obtain desired flexibility. In addition, too long a heating time also increases the possibility of forming an interdiffusion layer. Conversely, too short a heating time makes it difficult for porosification to occur, increasing the possibility of losing flexibility.

(Method of Evaluating Porous Nickel Thin Film)

[0046] As described above, the nickel thin film 3 which is manufactured by the method according to the embodiment has a property excellent in flexibility. To be more specific, it is possible to obtain the porous nickel thin film 3 with a "flexibility value" of 15.0 N/mm or less. Here, the "flexibility value" is a value determined using an evaluation method to

be described below.

[0047] Fig. 2 is a view of an external appearance of an evaluation apparatus 10 used in the evaluation method for the flexibility value. In addition, Fig. 3 is a schematic view showing the evaluation apparatus 10. As shown in Fig. 2 and Fig. 3, the evaluation apparatus 10 includes a body part 16, a stage 11, a pushing jig support 13, a measurement apparatus 18, a pushing jig 14, a subject supporting jig 12, and a drive mechanism 15. Note that the pushing jig 14 and the subject supporting jig 12 are detachable and illustrated only in Fig. 3, not in Fig. 2.

[0048] The stage 11 is provided to support the subject supporting jig 12, and is supported by the body part 16.

[0049] The subject supporting jig 12 is provided to support the nickel thin film 3 to be tested (see Fig. 3). The subject supporting jig 12 is detachably attached to the stage 11. Fig. 4 is a cross-sectional view schematically showing the subject supporting jig 12. The subject supporting jig 12 includes a pair of clamping members (12-1 and 12-2) . One clamping member 12-1 has an opening 17 provided therein. In addition, the other clamping member 12-2 has a hollow portion 16 provided at the position corresponding to the opening 17. Each of the opening 17 and the hollow portion 16 has the shape of a circle with a predetermined diameter of a. Note that the clamping member 12-2 may be provided with an opening instead of the hollow portion 16. Moreover, each clamping member (12-1 and 12-2) is provided with a screw thread (19-1 and 19-2), and it is thus possible to threadly engage the clamping member 12-1 with the clamping member 12-2 while clamping the nickel thin film 3. The center portion of the nickel thin film 3, that is, the region corresponding to the opening 17 is not in contact with the subject supporting jig 12. That is to say, the subject supporting jig 5 is configured to support the entire periphery of the nickel thin film 3, and an unsupported region with a closed shape corresponding to the opening 17 is formed in the center portion of the nickel thin film 3.

[0050] The pushing jig support 13 (see Fig. 2 and Fig. 3) is provided to support the pushing jig 14. The pushing jig support 13 is attached to the body part 16 so as to be movable in a direction perpendicular to the nickel thin film 3.

[0051] The drive mechanism 15 is attached to the body part 16 and has a function of causing the pushing jig support 13 to travel. The drive mechanism 15 is a motor, for example.

[0052] The pushing jig 14 has the shape of a rod. The pushing jig 14 is supported above the nickel thin film 3 by the pushing jig support 13 so as to extend in a direction perpendicular to the nickel thin film 3. In addition, one end (lower end) of the pushing jig 14 is set so as to be positioned right above the center of the opening 17 provided in the clamping member 12-1.

[0053] Fig. 5 is a schematic view showing an example of the pushing jig 14. As shown in Fig. 5, one end of the pushing jig 14 preferably has a shape corresponding to a portion of a sphere with a predetermined diameter of b.

[0054] The measurement apparatus 18 (see Fig. 3) has a function of detecting the force applied to the pushing jig 14 and the displacement amount of the pushing jig 14. To be more specific, the measurement apparatus 18 includes a load cell 18-1 and an encoder 18-2. The load cell 18-1 is provided between the pushing jig support 13 and the pushing jig 14 and has a function of detecting the force applied to the pushing jig 14. The encoder 18-2 is connected to the drive mechanism 15 and is configured to detect the displacement amount of the pushing jig support 13, that is, a displacement amount of the pushing jig 14.

[0055] Subsequently, a description is provided for the evaluation method of the present invention.

[0056] First, one supports a test piece of the nickel thin film 3 with the subject supporting jig 12 and places the subject supporting jig 12 on the stage 11. Also, one attaches the pushing jig 14 to the pushing jig support 13 via the load cell 18-1.

[0057] Next, the drive mechanism 15 moves the pushing jig support 13 downwards (toward the subject supporting jig 12). This pushes one end of the pushing jig 14 aligned with the center of the opening 17 perpendicularly into the nickel thin film 3, as shown in Fig. 6. The pushing jig 14 is pushed in until the nickel thin film 3 is torn. Here, the measurement apparatus 18 measures the force applied to the pushing jig 14 and the displacement amount of the pushing jig 14. The measurement results are stored in e.g. a computer (not shown) as data indicating the relationship between the force applied to the pushing jig 14 and the displacement amount of the pushing jig 14.

[0058] The flexibility value of the nickel thin film 3 is determined based on the obtained data. Here, in the specification, the "flexibility value" is a value expressed by a value (N/mm) which is the force (N) applied to the pushing jig divided by the displacement amount (mm) of the pushing jig. The smaller this value, the more flexible the nickel thin film 3 is. To be more specific, the flexibility value can be calculated by creating a graph with the horizontal axis representing the displacement amount and the vertical axis representing the force (test force) applied to the pushing jig 14, and by determining the gradient within a range where the linearity is good (for example, a region where the correlation coefficient R^2 determined by linear approximation is larger than 0.9).

[0059] The evaluation method described above makes it possible to properly evaluate the flexibility of the nickel thin film 3 with a thickness of 0.1 to 100 μm.

[0060] Note that the diameter a of the opening 17 provided in the clamping member 12-1 (see Fig. 4) is preferably 9 mm to 14 mm, more preferably 10 mm to 13 mm, and still more preferably 11 mm to 12 mm. Too small a diameter a makes it impossible to obtain a sufficient displacement amount for the test force, while a too large a diameter requires a large sample area.

[0061] Although not particularly limited, the shape of one end of the pushing jig 14 (see Fig. 5) is preferably a shape

corresponding to a portion of a sphere with a diameter of b, as already described. For example, if the shape of one end of the pushing jig 14 is a polygon, the pushing jig 14 touches the test piece at the vertexes. This increases the risk of tearing the test piece before the completion of the test because the test force concentrates at the vertexes. As a result, it becomes difficult to create a region with a high-linearity relationship in the test force-displacement amount graph. In addition, if the shape of one end of the pushing jig 14 is a flat-plate shape such as a flat plate circle, the test piece deforms to make an acute angle at an edge of this flat-plate shape. For this reason, it becomes difficult to obtain a high-linearity relationship. As opposed to the above, if the shape of one end of the pushing jig 14 has a shape corresponding to a portion of a sphere, one obtains an effect of pushing the test piece with a surface. To be more specific, when the pushing jig 14 is being pushed in, the test piece is smoothly stretched while making an obtuse angle. This helps to obtain a higher-linearity relationship.

[0062] The diameter b is preferably 5 mm to 10 mm, more preferably 6 mm to 9 mm, and still more preferably 7 mm to 8 mm. Too small a diameter b means that the test piece is pressed at a point, increasing the risk that the test piece is easily torn. On the other hand, too large a diameter b means that the subject supporting jig 12 also needs to be large, increasing the necessary sample area.

[0063] Furthermore, the ratio of the diameter b to the diameter a of the opening 17 (diameter b/diameter a) is preferably 0.3 to 0.9, more preferably 0.4 to 0.8, and still more preferably 0.5 to 0.7. The ratio of the diameter b to the diameter a within such ranges helps to obtain a high-linearity relationship.

[0064] The push rate of the pushing jig 14 is preferably 0.1 mm/min to 10.0 mm/min, more preferably 0.5 mm/min to 5.0 mm/min, and still more preferably 1.0 mm/min to 2.0 mm/min. Too low a push rate requires a long time test. On the other hand, too high a push rate increases the risk of breaking the test piece, and the test piece is likely to be broken before a region with a high linearity is sufficiently obtained.

[0065] Subsequently, Examples are described for the purpose of explaining the present invention in further detail.

[Example 1]

[0066] An SUS substrate was prepared as the conductive substrate 1 being the undercoat. The nickel plated film 2 was formed on this conductive substrate 1 by electroplating. Here, the aqueous solution used as the electroplating bath contained 600 g/L of nickel sulfamate, 10 g/L of nickel chloride, 40 g/L of boric acid, and 10 ml/L of anionic surfactant (sodium dodecylbenzenesulfonate). The pH of the plating bath was 3.5, and the bath temperature was 60°C. The electroplating was carried out by pulse plating. Pulse plating was carried out under the conditions that the average current density was 5.9 A/dm^2 and the ratio (ton/toff) was 1.4. Next, the nickel plated film 2 was peeled off the conductive substrate 1. Furthermore, heat treatment was carried out at 500°C on the nickel plated film 2 for 60 minutes in the atmosphere, and the nickel thin film 3 according to Example 1 was obtained. The thickness of the obtained nickel thin film 3 was 5 μm.

[Example 2]

[0067] The nickel thin film 3 according to Example 2 was obtained using the same method as in Example 1, but the heat treatment time was 120 minutes.

[Comparative Example 1]

[0068] The nickel thin film 3 according to Comparative Example 1 was obtained using the same method as in Example 1, but the heat treatment was not carried out.

[Comparative Example 2]

[0069] The nickel thin film 3 according to Comparative Example 2 was obtained using the same method as in Example 1, but the heat treatment was not carried out. Here, the solution used as the electroplating bath had 350 g/L of nickel sulfate, 60 g/L of nickel chloride, 30 g/L of trisodium citrate dissolved therein (no surfactant contained). The pH of the plating bath was 4.6 and the bath temperature was 60°C. The plating conditions included a constant current of 0.1 A.

[Comparative Example 3]

[0070] A nickel film with a thickness of 10 μm manufactured by rolling was prepared as the nickel thin film according to Comparative Example 3.

[Comparative Example 4]

[0071] A Cu film with a thickness of 10 μm manufactured by rolling was prepared as the metal film according to Comparative Example 4.

[Comparative Example 5]

[0072] An Al film with a thickness of 10 μm manufactured by rolling was prepared as the metal film according to Comparative Example 5.

[Comparative Example 6]

[0073] An attempt was made to obtain the nickel thin film according to Comparative Example 6 by carrying out heat treatment on the nickel thin film according to Comparative Example 2 under the same conditions as in Example 1. However, the nickel thin film according to Comparative Example 2 after the heat treatment was brittle due to oxidation and no longer maintained its shape.

[0074] Subsequently, evaluated were the flexibilities of the nickel thin films and the metal films obtained in Examples 1 and 2 and Comparative Examples 1 to 5. To be specific, the relationship between the test force and the displacement amount was measured by use of the evaluation apparatus 10 described in Figs. 2 to 6.

[0075] More specifically, each of the test pieces was cut to form a circle with a diameter of 20 mm. Then, the test piece was clamped and secured on the stage 11 by use of the pair of clamping members (12-1 and 12-2) which have the opening 17 and the hollow portion 16 both with a diameter of 12 mm. Further, a jig having on one end a shape corresponding to a portion of a sphere with a diameter of 7 mm was prepared as the pushing jig 14, and was attached to the pushing jig support 13. The pushing jig support 13 was moved toward the pair of clamping members 12 at a rate of 1 mm/min. Thereby, one end of the pushing jig 14 aligned with the center of the opening 17 was caused to touch the test piece. Moreover, the pushing jig 14 was pushed in until the test piece was torn, and the relationship between the displacement amount of the pushing jig 14 and the test force (force applied to the pushing jig 14) was measured with the measurement apparatus 18.

[0076] Fig. 7 is a graph showing measurement results. In Fig. 7, the correspondence relationship between the curves and Examples 1 to 2 and Comparative Examples 1 to 5 is as follows:

Example 1: Curve "1"
Example 2: Curve "2"
Comparative Example 1: Curve "3"
Comparative Example 2: Curve "4"
Comparative Example 3: Curve "5"
Comparative Example 4: Curve "6"
Comparative Example 5: Curve "7"

[0077] For each of the graphs in Fig. 7, a portion of sudden decrease in the test force corresponds to a point at which the test piece is torn (hereinafter referred to as a breaking point) . In any of Examples 1 and 2 and Comparative Examples 1 to 5, a high-linearity relationship between the displacement amount and the test force is obtained within the region from the origin to the breaking point. This indicates that the evaluation method of the present invention properly reflects the flexibility of the test piece.

[0078] As shown in Fig. 7, the nickel thin films 3 according to Examples 1 and 2 have larger displacement amounts until the test piece is broken compared to the nickel thin films and the metal films according to Comparative Examples 1 to 5. Furthermore, as compared to Comparative Examples 1 to 5, Examples 1 and 2 have a larger area of the region surrounded by the origin, the breaking point, and the point on the X-axis corresponding to the breaking point, i.e. a larger amount of work with respect to elongation. This indicates that Examples 1 and 2 have higher elongation properties, higher flexibility, and higher mechanical strengths compared to Comparative Examples 1 to 5.

[0079] Fig. 8 is a graph showing results of calculating "flexibility values." Note that the "flexibility values" were calculated by determining a range where the linearity is good (correlation coefficient $R^2 > 0.9$ in linear approximation) in the graph shown in Fig. 7 and by determining the gradient. As shown in Fig. 8, Examples 1 and 2 have smaller "flexibility values" compared to Comparative Examples 1 and 2. To be more precise, it is understood that a nickel thin film 3 with a high elongation property and high flexibility can be obtained by carrying out electroplating with a plating bath containing a surfactant, and by removing the surfactant through heat treatment. Moreover, it is understood that the nickel thin films 3 of Examples 1 and 2 have smaller flexibility values compared to the metal films of Comparative Example 3 and 4, and have higher elongation properties and higher flexibility compared to the nickel film and the Cu film obtained by rolling.

[0080] Furthermore, while the flexibility values of Examples 1 and 2 are larger than that of Comparative Example 5, the test piece of Comparative Example 5 is torn at a displacement amount much smaller than those in Examples 1 and 2, as shown in Fig. 7. To be more specific, it is understood that the nickel thin films 3 according to Examples 1 and 2 greatly surpass in mechanical strength the Al film obtained by rolling.

[0081] What is more, while the nickel plated film according to Comparative Example 6 did not maintain its shape when heat-treated, the shapes were maintained after heat treatment and flexibility was improved as well in Examples 1 and 2. It can be said from the above description that the results of Examples 1 and 2 were unexpected.

Claims

1. A porous nickel thin film having a flexibility value of 15.0 N/mm or less, the flexibility value being a value measured by a method comprising the steps of:

   supporting an entire periphery of the nickel thin film with a subject supporting jig so as to form an unsupported region with a closed shape in the nickel thin film;
   measuring a relationship between a force applied to a pushing jig and a displacement amount of the pushing jig by pushing one end of the pushing jig against the unsupported region perpendicularly to the nickel thin film; and
   obtaining a value (N/mm) by dividing the force (N) applied to the pushing jig by the displacement amount (mm) of the pushing jig, as the flexibility value.

2. The porous nickel thin film according to claim 1, having a thickness of 0.1 to 100 μm.

3. A method for manufacturing a porous nickel thin film, comprising the steps of:

   forming a nickel plated film on a conductive substrate by use of a nickel electroplating bath containing a nickel salt and a surfactant; and
   heat-treating the nickel plated film so as to burn and remove the surfactant taken in the nickel plated film.

4. The method according to claim 3, wherein
   the porous nickel thin film has a flexibility value of 15.0 N/mm or less, and the flexibility value is a value measured by a method comprising the steps of:

   supporting an entire periphery of the nickel thin film with a subject supporting jig so as to form an unsupported region with a closed shape in the nickel thin film;
   measuring a relationship between a force applied to a pushing jig and a displacement amount of the pushing jig by pushing one end of the pushing jig against the unsupported region perpendicularly to the nickel thin film; and
   obtaining a value (N/mm) by dividing the force (N) applied to the pushing jig by the displacement amount (mm) of the pushing jig, as the flexibility value.

5. The method according to claim 3 or 4, wherein
   the surfactant contains an anionic surfactant.

6. The method according to claim 5, wherein
   the anionic surfactant contains a compound selected from the group consisting of a polyoxyalkylene alkyl ether sulfate, a polyoxyalkylene alkyl ether carboxylate, and an alkylbenzene sulfonate.

7. The method according to any one of claims 3 to 6, wherein
   the step of forming a nickel plated film includes a step of carrying out pulse electroplating.

8. The method according to any one of claims 3 to 7, wherein
   the conductive substrate is a Ti substrate, a Cu substrate, an SUS substrate, a glass given electrical conductivity, or a resin given electrical conductivity.

9. The method according to any one of claims 3 to 8, further comprising a step of peeling the porous nickel thin film off the conductive substrate.

FIG.1A

FIG.1B

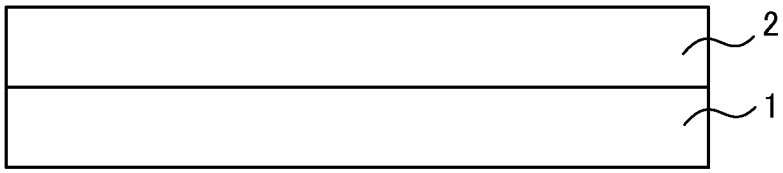


FIG.1C

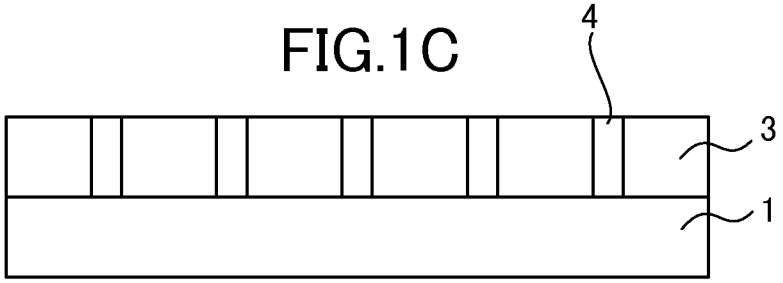


FIG.1D

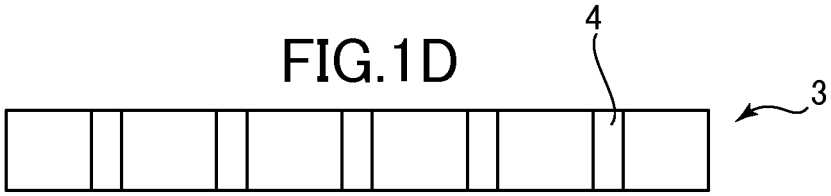


FIG.2

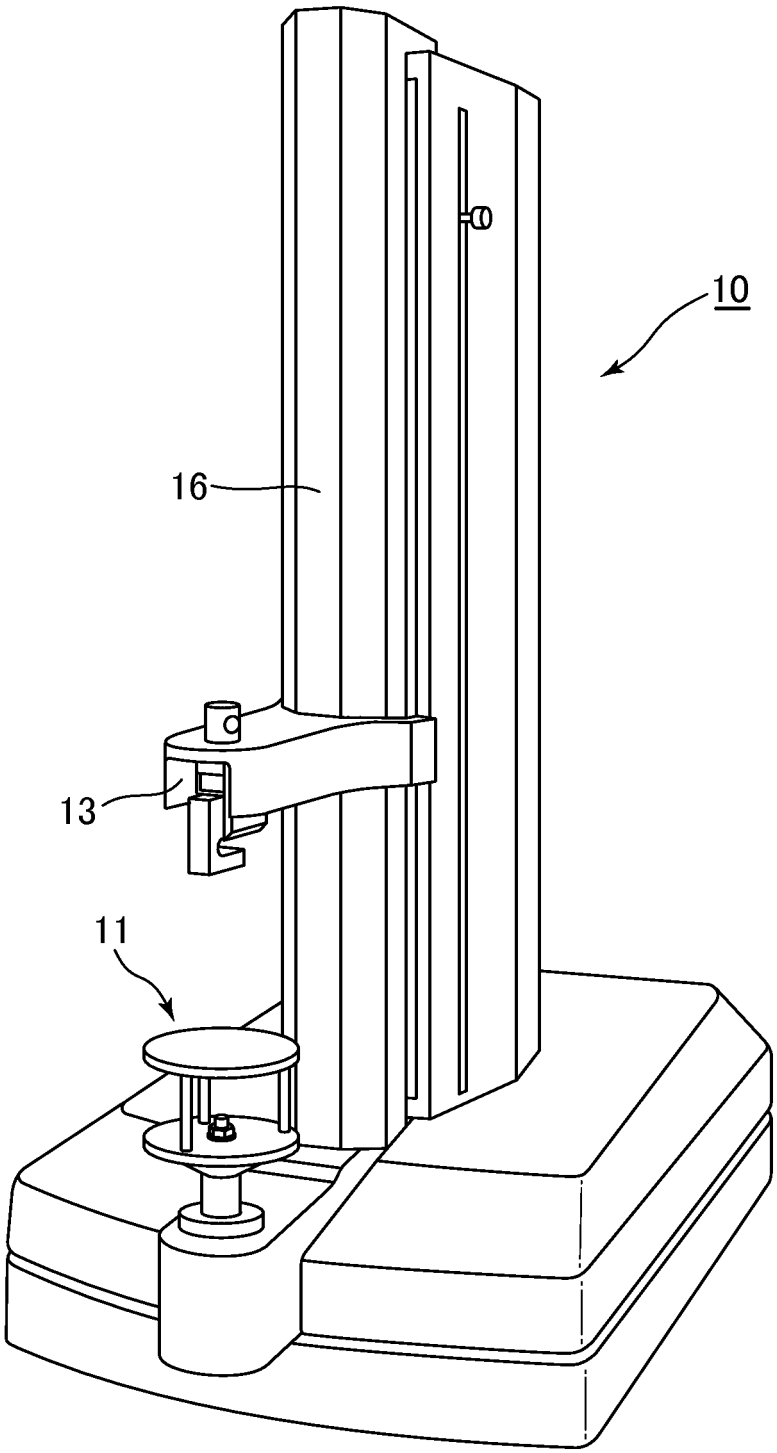


FIG.3

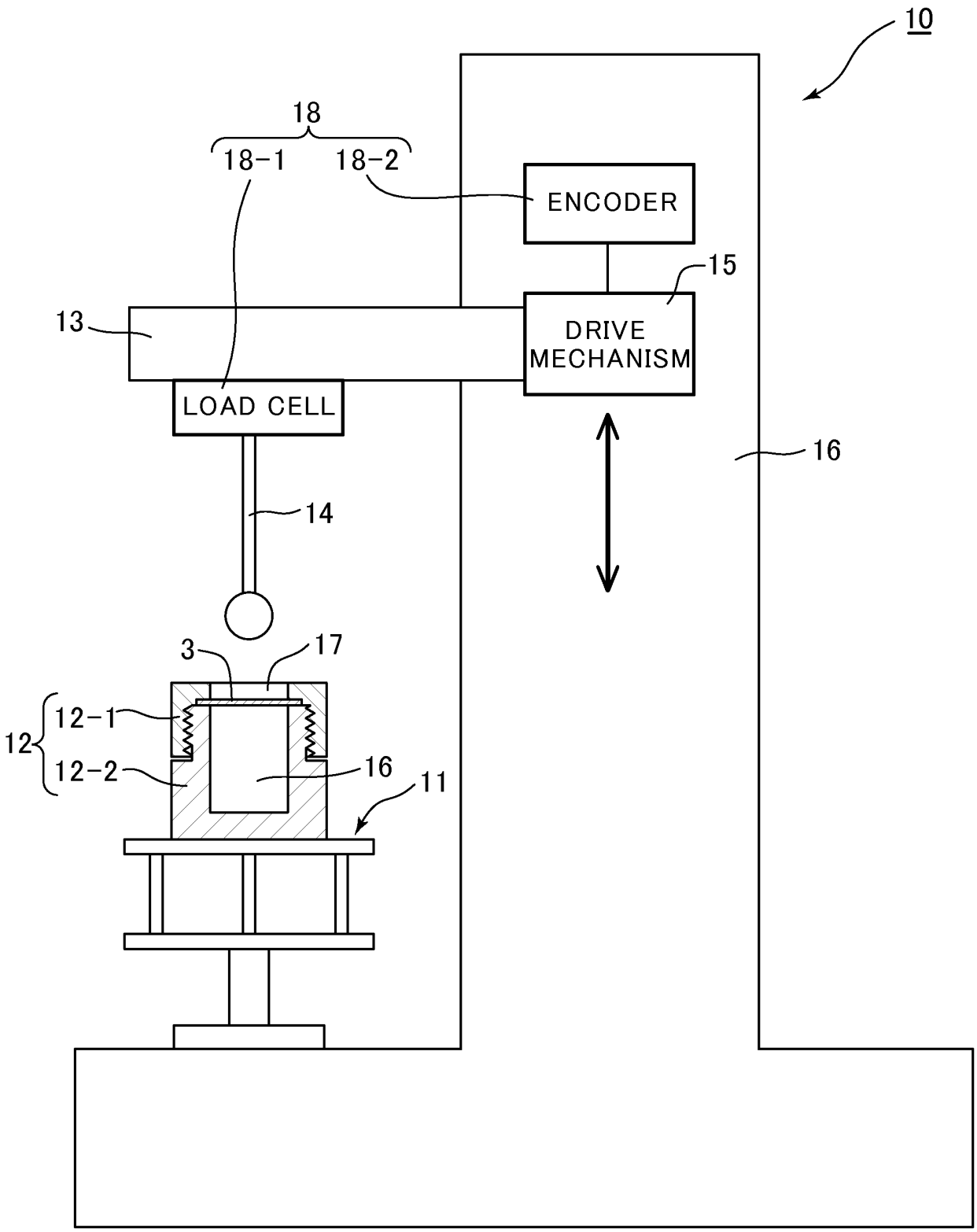

10
18
18-1
18-2
ENCODER
15
13
DRIVE MECHANISM
LOAD CELL
16
14
3
17
12
12-1
12-2
16
11

FIG.4

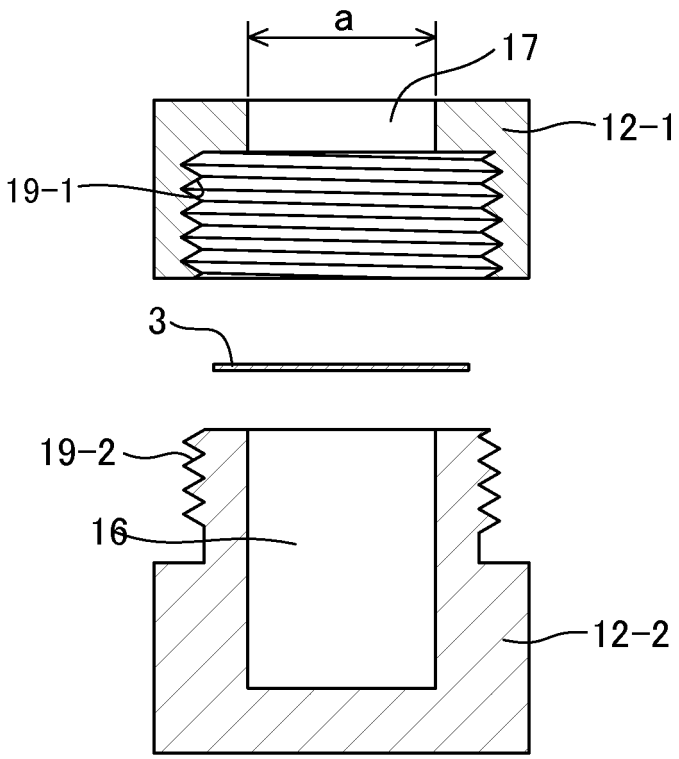


FIG.5

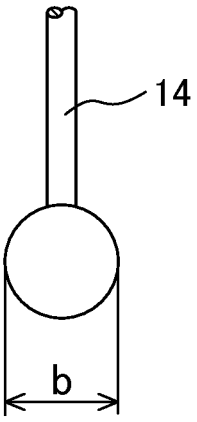


FIG.6

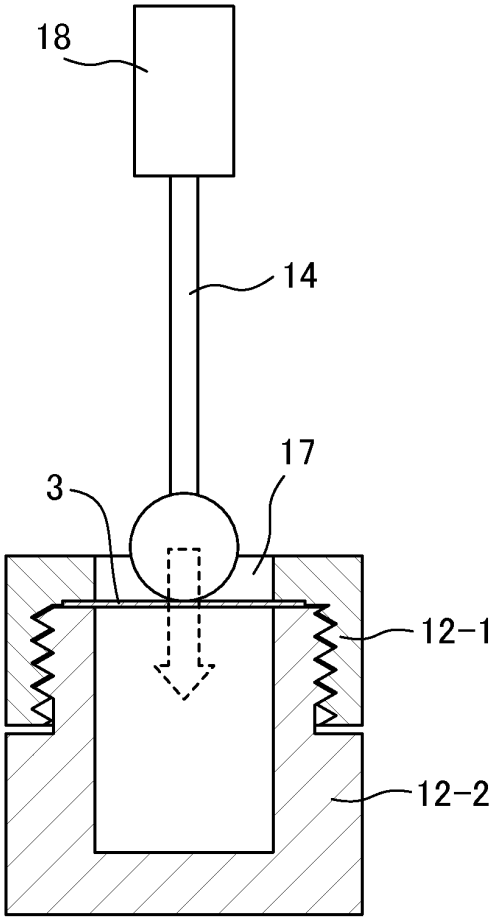

18
14
17
3
12-1
12-2

FIG.7

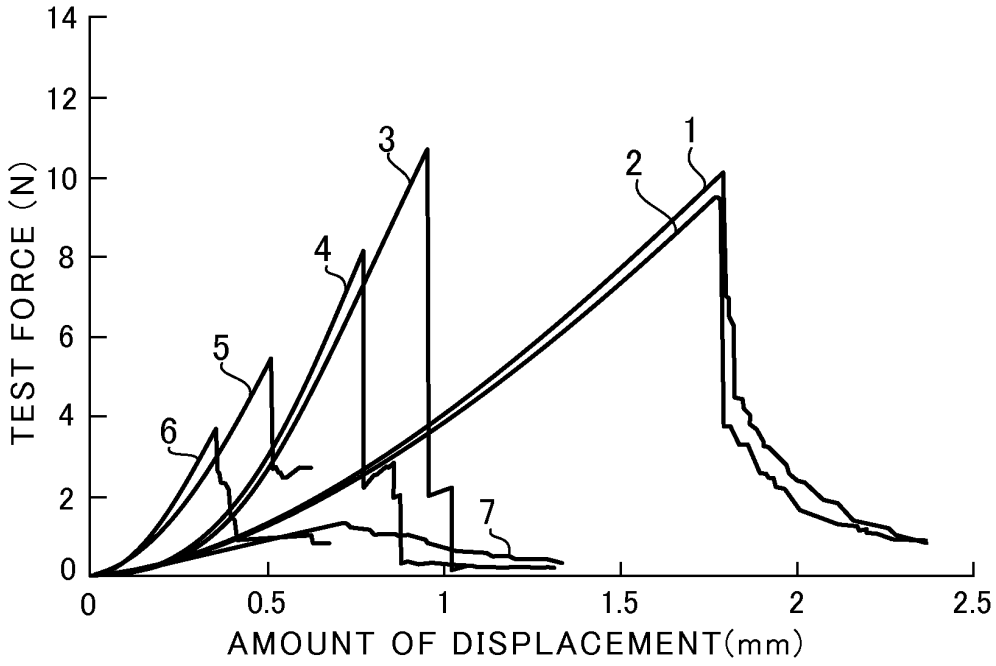
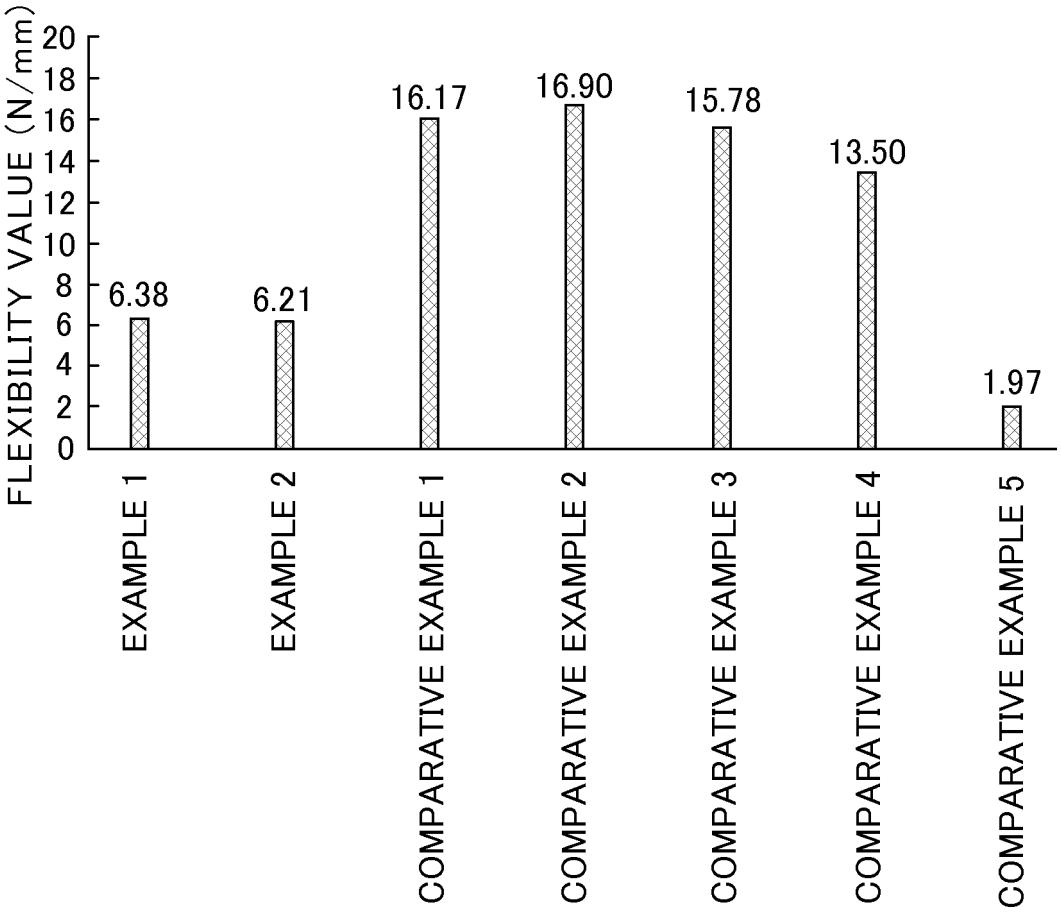

TEST FORCE (N)
AMOUNT OF DISPLACEMENT(mm)
0
2
4
6
8
10
12
14
0
0.5
1
1.5
2
2.5
1
2
3
4
5
6
7

FIG.8


FLEXIBILITY VALUE (N/mm)
0
2
4
6
8
10
12
14
16
18
20
6.38
6.21
16.17
16.90
15.78
13.50
1.97
EXAMPLE 1
EXAMPLE 2
COMPARATIVE EXAMPLE 1
COMPARATIVE EXAMPLE 2
COMPARATIVE EXAMPLE 3
COMPARATIVE EXAMPLE 4
COMPARATIVE EXAMPLE 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/082608

A. CLASSIFICATION OF SUBJECT MATTER
C25D1/08(2006.01)i, *C25D1/00*(2006.01)i

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)
C25D1/08, C25D1/00

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 1996-2016
Kokai Jitsuyo Shinan Koho 1971-2016 Toroku Jitsuyo Shinan Koho 1994-2016

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.
A	JP 6-065779 A (Ikex Industry Co., Ltd.), 08 March 1994 (08.03.1994), claims; paragraphs [0018] to [0037] (Family: none)	1-9
A	JP 2010-121194 A (Okuno Chemical Industries Co., Ltd.), 03 June 2010 (03.06.2010), claims; paragraphs [0032] to [0047] (Family: none)	1-9
A	JP 2012-041608 A (Sumitomo Electric Toyama Co., Ltd.), 01 March 2012 (01.03.2012), claims; paragraphs [0027] to [0037] (Family: none)	1-9

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 November 2016 (24.11.16)	06 December 2016 (06.12.16)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/082608

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2013-014819 A (Murata Mfg. Co., Ltd.), 24 January 2013 (24.01.2013), claims; paragraphs [0025] to [0027], [0042], [0043] (Family: none)	1-9
P,X	JP 6014920 B1 (Sanno Co., Ltd.), 26 October 2016 (26.10.2016), claims; paragraphs [0014], [0019], [0024] (Family: none)	1-9
P,X	JP 2016-094659 A (Sanno Co., Ltd.), 26 May 2016 (26.05.2016), claims; paragraphs [0012] to [0014] (Family: none)	1-9

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 4411409 B **[0002] [0003]**