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(54) **Antibacterial amorphous alloy highly resistant to oxidation, discoloration, and corrosion, fabric coated with amorphous alloy, and insole.**

(57) A Cu amorphous alloy of any of the compositions shown in (1) to (4) below. A fabric coated with a Cu amorphous alloy of any of the compositions shown in (1) to (4) below by sputtering. An insole having a copper-containing amorphous alloy-coated non-woven fabric interposed between gas-pervious layers of polyvinylidene chloride.

(1) A Cu-containing amorphous alloy comprising not less than 5 atomic % of Ta and/or not less than 15 atomic % of Nb and Ti and Ni and the balance substantially of Cu and characterized by the fact that the total content of Ta and Nb and Ti is in the range of from 30 to 62.5 atomic %, the content of Ni in the range of from 0.6 to 4 times the total content of Ta and Nb, and the content of Cu in the range of from 0.6 to 4 times the content of Ti.

(2) A Cu-containing amorphous alloy comprising from 15 to 85 atomic % of Ta and/or Nb and the balance substantially of Cu.

(3) A Cu-containing amorphous alloy comprising not less than 1 atomic % of Ta, Ti and/or Zr, and the balance substantially of Cu and characterized by the fact that the total content of Ta and Ti and Zr is in the range of from 15 to 85 atomic %.

(4) A Cu-containing amorphous alloy comprising not less than 1 atomic % of Ta and Na, Ti and/or Zr, and the balance substantially of Cu and characterized by the fact that the total content of Ta and Nb and Ti and/or Zr is in the range of from 15 to 85 atomic %.

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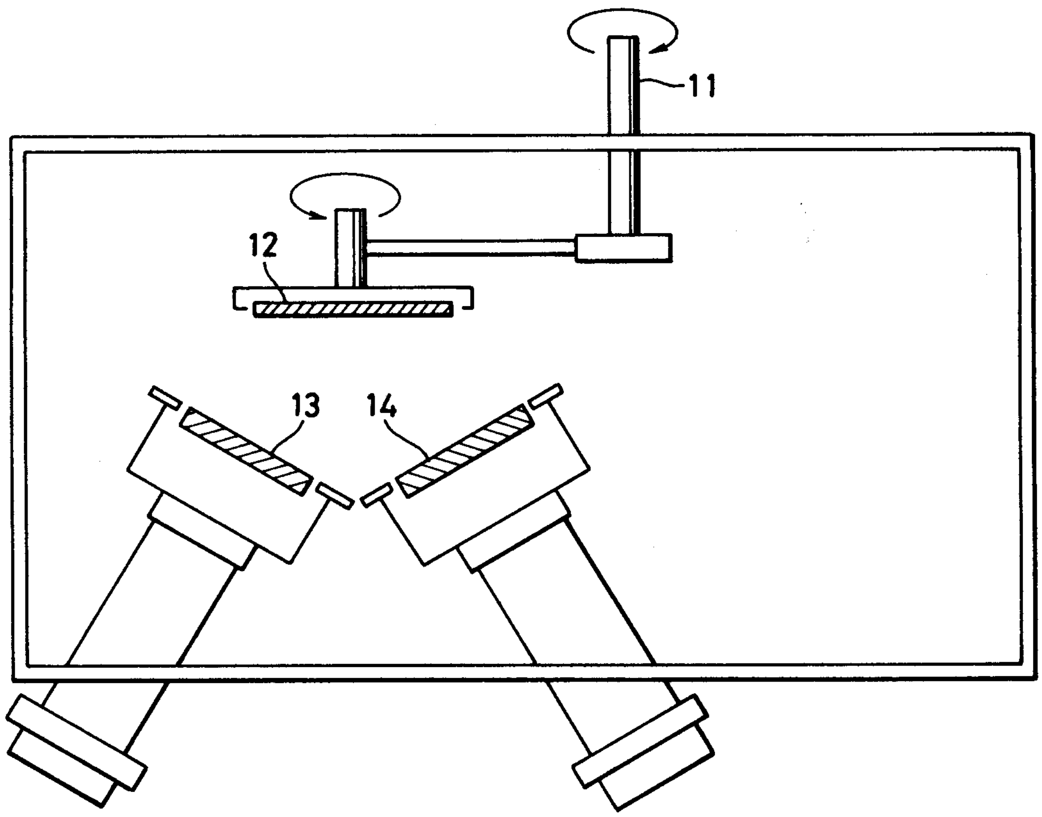
FIG.7



BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

This invention relates to an antibacterial amorphous alloy highly resistant to oxidation, discoloration, and corrosion, i.e. an amorphous alloy exhibiting an outstanding antibacterial property to fungi and bacteria and, at the same time, and excelling in resistance to oxidation, discoloration, and corrosion, a fabric coated with the amorphous alloy, and an insole made of the fabric and consequently endowed with both antibacterial property and corrosionproofness.

DESCRIPTION OF THE PRIOR ART

It has been known for a long time that copper (Cu) and silver (Ag) ions are fungicidally active. The use of a copper-containing coating material on a ship's bottom to preclude adhesion thereto of algae and barnacles and the use of silver ions for the disinfection of bathhouses may be cited as familiar examples. The use of a material produced by sintering a mixture of copper and stainless steel powder for the protection of various structures against deposition of marine organisms has been also known to the art.

This practice is said to be ascribable to the fact that these metal ions, owing to their catalytic action, continuously generate active oxygen piecemeal to obstruct energy metabolism in microorganisms and these ions in themselves are capable of migrating into microorganisms and destroying them.

The copper, however, is deficient in corrosionproofness and susceptible of oxidation and, therefore, suffers ready conversion of the antibacterial Cu^{+} ion into a compound possessed of a very low antibacterial ability. The silver suffers poor feasibility because it is susceptible of oxidation and discoloration, sparingly capable of ionization, and expensive.

The athlete's foot and the offensive odor emanating from filthy feet are believed to be caused by fungi (dermatomycosis) and bacteria (staphylococci) which infest feet in shoes. It is known that copper manifests a literally excellent antibacterial action to these fungi and bacteria which steal growth in shoes.

The insoles which are made of copper foil, for example, and intended to utilize the antibacterial action of copper have been proposed for the protection of feet against athlete's foot and the offensive odor from filthy feet. They are partly available in the market.

Japanese Patent Publication SHO 52(1977)-18,256, for example, discloses insoles which are made of a copper sheet. Japanese Patent Application Disclosure SHO 63(1988)-158,002 discloses insoles which are coated with a copper layer 50 to 100 μm in thickness deposited by flame spraying. Japanese Utility Model Application Disclosure SHO 62(1987)-17,905 teaches insoles which are covered with a copper layer 50 to 10 μm in thickness deposited by plating.

Of the conventional insoles mentioned above, those using a copper sheet [Japanese Patent Publication SHO 52(1977)-18,256] suffer poor sensation of skin touch because the copper sheet lacks flexibility. Those insoles of Japanese Patent Application Disclosure SHO 63(1988)-158,002 and Japanese Utility Model Application Disclosure SHO 63(1988)-158,002 and Japanese Utility Model Application Disclosure SHO 62-(1987)-17,905 are likewise incapable of acquiring fully satisfactory flexibility. Incidentally, copper betrays poor corrosionproofness in spite of its outstanding antibacterial property. During a protracted use, therefore, the conventional insoles suffer oxidation of copper followed by deterioration of quality, discoloration, and loss of the antibacterial property and a good outside appearance.

SUMMARY OF THE INVENTION

An object of this invention is to solve the problem of the conventional insoles described above and an alloy using inexpensive copper as an antibacterial component, i.e. an antibacterial amorphous alloy exhibiting outstanding resistance to oxidation, discoloration, and corrosion.

Another object of this invention is to solve the problems of the conventional insoles described above and provide an amorphous alloy-coated fabric combining an antibacterial property and corrosionproofness and useful advantageously in insoles.

Still another object of this invention is to solve the problems of the conventional soles and provide an insole which combines an antibacterial property and corrosionproofness.

The other objects and characteristic features of the present invention will become apparent from the following detailed description of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a type cross section illustrating the surface state of an amorphous alloy-coated of the present invention placed in a corrosive atmosphere.

Fig. 2 is a type cross section illustrating the surface of an amorphous alloy-coated of the present invention placed in a corrosive atmosphere.

Fig. 3 is a type cross section illustrating the surface state of an amorphous alloy-coated fabric of this invention immediately after the sputtering of Cu amorphous alloy.

Fig. 4 is a graph showing the results of X-ray photoelectron spectroscopic analysis of sample surface.

Fig. 5 is a graph showing the polarization characteristic of Cu containing amorphous alloy.

Fig. 6 is a graph showing the relation between the Ta content and the corrosionproofness of a Cu containing amorphous alloy.

Fig. 7 is a schematic structural diagram illustrating one example of the sputtering device ideal for the manufacture of an amorphous alloy-coated fabric according with the present invention.

Fig. 8 is a schematic structural diagram illustrating another example of the sputtering device ideal for the manufacture of an amorphous alloy-coated fabric according with this invention.

Fig. 9 is a perspective view illustrating one example of the insole using an amorphous alloy-coated fabric according with the present invention.

Fig. 10 is a magnified cross section taken through Fig. 9 along the line X-X.

Fig. 11 is a magnified cross section taken through Fig. 9 along the line X-X.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The antibacterial amorphous alloy of this invention highly resistant to oxidation, discoloration, and corrosion is an alloy which consists of not less than 5 atomic percent of Ta and/or not less than 15 atomic percent of Nb, Ti, and Ni, and the balance substantially of Cu. This alloy is characterized by the fact that the total content of Ta and/or Nb and Ti is in the range of from 30 to 62.5 atomic percent, the content of Ni is from 0.6 to 4 times the content of Ta and/or Nb, and the content of Cu is from 0.6 to 4 times the content of Ti.

The amorphous alloy-coated fabric of the present invention is characterized by the fact that this fabric is produced by sputter coating a substratal fabric with an amorphous alloy consisting of not less than 5 atomic percent of Ta and/or not less than 15 atomic percent of Nb, Ti, and Ni, and the balance substantially of Cu and characterized by the fact that the total content of Ta and/or Nb and Ti is in the range of from 30 to 62.5 atomic percent, the content of Ni is from 0.6 to 4 times the content of Ta and/or Nb, and the content of cu is from 0.6 to 4 times the content of Ti.

The insole of the present invention is characterized by comprising a non-woven fabric coated with a copper-containing amorphous alloy (hereinafter referred to briefly as "Cu amorphous alloy") and gas-pervious layers of polyvinylidene chloride deposited one each on the opposite surfaces of the non-woven fabric.

As one of the characteristic features of an amorphous alloy, high freedom of design manifested by the fact that an amorphous alloy possessing a desired function can be manufactured by the incorporation of an alloy element possessed of the particular function may be cited.

The amorphous alloy produced by alloying Cu, an element excellent in the antibacterial property and yet susceptible of oxidation and corrosion, with an element excelling in corrosionproofness, therefore, produces a designed behavior even when the combination of component elements is not attained in a crystal alloy. As a result, the amorphous alloy derives the antibacterial ability from Cu and, at the same time, the outstanding resistance to oxidation from the corrosionproofing element incorporated in the alloy. The otherwise possible discoloration, degradation, and loss of the antibacterial property due to the deterioration by oxidation can be precluded.

It is said that the antibacterial property of Cu is manifested most effectively when it is in the ionic state of Cu^{+} but that this property is not effective when the Cu is in the metallic state of Cu^{0} or in the ionic state of Cu^{2+}. In the case of Cu in the state of crystal metal, the bulk surface initially exists in the state of Cu^{0} to Cu^{+} (Cu_2O) and, on elapse of time, converts itself into Cu^{2+} (CuO) or some other compound. As a result, the antibacterial property is gradually lost along the course of time.

In contrast, the Cu-containing amorphous alloy exhibits an outstanding antibacterial property because the Cu in the passive film formed on the surface of this coated alloy exists in the state of Cu^{+} and the Cu^{+} ion migrates from within this film to the surface thereof.

The operation and effect of this invention will be described below with reference to the Cu amorphous alloy applied by sputtering in the form of a coating on a non-woven fabric of nylon. Immediately after the sputtering, an amorphous alloy matric phase 2 is formed on a non-woven fabric 1 as illustrated in Fig. 3.

Once the coated non-woven fabric 1 is placed in a corrosive atmosphere, the Cu in the surface of the amorphous alloy matrix phase 2 is preferentially dissolved and the corrosionproofing element (mainly Ta in the present case) is concentrated on the matrix phase surface as illustrated in Fig.1 to form a strong oxide protective film, namely a passive film 3 (which passive film is formed mainly of Ta_2O_5 or TiO_2; the alloy elements, therefore, exist in the ionic states of Ta^{5+}, Ti^{4+}, Cu^{+}), with the result that the coated non-woven fabric 1 will acquire improved corrosionproofness. Otherwise, a surface layer 4 of Cu_2O containing Cu^{+} ion is formed further on the passive film 3 as illustrated in Fig. 2, with the result that the coated non-woven fabric 1 will manifest an antibacterial property.

This behavior may be logically explained by a postulate that since the passive film 3 is depleted of Cu, the Cu^{+} ion is supplied from the amorphous alloy matrix phase 2 to the passive film 3 and further passed through the film 3 and thence dissolved per se or eventually converted into the oxide, Cu_2O. It is, therefore, the Cu^{+} ion that effectively acts on some fungi and bacteria.

Fig. 4 shows the results of X-ray photoelectron spectroscopic analysis of the state of Cu ion on a surface performed on the non-woven fabric coated with an amorphous alloy according with the present invention and on the crystal metal copper. In the determination of the Cu2P photoelectric binding energy on the surface of a sample, the curve A representing the data of the amorphous alloy-coated on non-woven fabric shows no satellite peak of Cu2P indicating that the Cu ion on the surface was in the state of a monovalent oxide, Cu_2O (Cu^{+}). The curve B representing the data of the metallic copper indicates that the Cu (Cu^0) which was initially in the metallic state was gradually oxidized into a monovalent oxide (Cu_2O: Cu^{+}). When this monovalent oxide underwent further oxidation it eventually converted itself into CuO (Cu^{2+}) possessing a satellite peak as indicated by the curve C.

Table 1 shows the results of the BCOD absorption spectal analysis performed to determine the amount of Cu ion dissolved out in 200 ml of an 5 vol% NaCl solution from an amorphous alloy-coated non-woven fabric. From the results, it is noted that the Cu ion was dissolved out of the amorphous alloy in a sizable amount. Even after this test, the surface of the amorphous alloy-coated non-woven fabric retained a metallic gloss and betrayed absolutely no sign of corrosion.

Table 1

Composition of amorphous alloy (atomic %)	Cu-40Ti-10Ta
Temeprature and number of days of immersion	Room temperature, seven days
Amount dissolved out (mg/100 cm^2)	0.36

The amorphous alloy-coated fabric of this invention, as described above, is enabled to derive the antibacterial ability of Cu from the Cu amorphous alloy and, at the same time, acquire outstanding resistance to oxidation and corrosion owing to the corrosionproofing element contained in the amorphous alloy and is further prevented from discoloration and degradation due to oxidative deterioration and also from loss of the antibacterial property.

Now, the present invention will be described more specifically below. The term "alloy" as used in the present invention refers to a combination of component elements which collectively account for 100 atomic %. Hereinafter, an amorphous alloy of a composition conforming to the present invention may be referred occasionally to as "Cu amorphous alloy."

The proportions of the component elements in the composition contemplated in this invention are limited for the following reasons.

In the amorphous alloys set forth in claims 1 to 4, the Cu is an element responsible for the antibacterial property. From the standpoint of the antibacterial activity, the Cu content is desired to be in the range of from 30 to 80 atomic %. In all the component elements of the amorphous alloy, Ta exhibits the most satisfactory corrosionproofness. The Ta content is desired to be in the range of from 10 to 20 atomic %.

For the present invention, the Cu amorphous alloy is desired to comprise 30 to 80 atomic % of Cu, 10 to 20 atomic % of Ta, and the balance of such an element as Ti. If the Cu content exceeds the upper limit of the range mentioned above, the Cu amorphous alloy suffers an obstruction to the formation of an amorphous texture and deficiency in corrosionproofness. Conversely, if the Cu content falls short of the lower limit of the range, the amorphous alloy suffers an increase of cost because of increased Ta and Ti contents. Though no Ta in excess of 20 atomic % is required from the viewpoint of corrosionproofness, an excess of the Cu content has no adverse effect on the Ta antibacterial property of the Cu amorphous alloy so long as the Cu content is in the range thereof mentioned above.

In the Cu amorphous alloy set forth in claim 1, Ta, Nb, and Ti are invariably elements which form a protective coating in a non-oxidative acid and give birth to the corrosionproofness of the alloy. In the elements mentioned above, Ta is most effective in the behavior. So long as the Ta content is not less than 5 atomic %, the produced Cu amorphous alloy exhibits fully satisfactory corrosionproofness even in concentrated hydrochloric acid when the total content of Ta and Ti or Ta, Ti, and Nb is 30 atomic %. The Nb is the most effective element next to Ta in corrosionproofing the Cu amorphous alloy. So long as the Nb content is not less than 15 atomic %, the Cu amorphous alloy possesses fully satisfactory corrosionproofness even in concentrated hydrochloric acid when the content of Ti or the total content of Ti and Ta is 30 atomic % or more.

When Ni and Cu are combined with any of Ta, Nb, and Ti in a proper proportion, the produced alloy acquires an amorphous texture. Among other conceivable combinations, Ta and Nb easily produce an amorphous alloy in combination with Ni and Ti easily produces an amorphous alloy in combination with Cu. When the alloy of this invention is a four- or five-component alloy including Ta and/or Nb, Ti, Ni, and Cu, the Ni content is from 0.6 to 4 times the Ta content, or the Nb content, or the total content of Ta and Nb where these two elements are simultaneously contained. The Cu substantially accounts for the balance of the alloy. Specifically, the Cu content is from 0.6 to 4 times the Ti content. The total content of Ta and/or Nb and Ti, therefore, is not more than 62.5 atomic %.

Optionally, the amorphous alloy set forth in claim 1 may further incorporate therein not more than 5 atomic % of Mo, W, or Zr without jeopardizing the objects of the present invention.

In the amorphous alloy set forth in claims 2 to 4, Zr similarly to Ta, Nb, and Ti contributes in combination with Cu to the formation of an amorphous texture. In order for the alloy produced by the sputtering technique to acquire an amorphous texture, it is required to incorporate therein at least one element selected from the group consisting of Ta, Nb, Zr, and Ti in a proportion in the range of from 15 to 85 atomic %. The Cu-Nb binary alloys and all the Ta-containing amorphous alloys, except for the Cu-Ti, Cu-Zr, Cu-Ti-Zr, Cu-Nb-Ti, Cu-Nb-Zr, and Cu-Nb-Ti-Zr alloys which are Ta-excluding alloys of Ti and/or Zr and Cu and alloys of Ti and/or Zr and Nb and Cu, are only producible by the sputtering technique. They are the alloys which are set forth in claims 2 to 4. Since the alloys containing Ta only in a proportion of less than 1 atomic % and the alloys containing Ta and Nb in a total amount of less than 1 atomic % are regarded as equalling alloys of Ti and/or Zr and Cu containing substantially no Ta and alloys of Ti and/or Zr and Nb and Cu, i.e. the Cu-Ti, Cu-Zr, Cu-Ti-Zr, Cu-Nb-Ti, Cu-Nb-Zr, and Cu-Nb-Ti-Zr alloys, the alloys set forth in claims 3 and 4 are defined as containing Ta in a proportion of not less than 1 atomic % of Ta or Ta and Nb in a total proportion of not less than 1 atomic %.

Incidentally, Ta, Nb, Zr, and Ti are elements which invariably form a protective film in a non-oxidative acid and give birth to the corrosionproofness of the alloy. Zr, Ti, Nb, and Ta are increasingly more effective in the order mentioned and, therefore, are different in corrosionproofness. The alloys set forth in claims 2 to 4 also exhibit fully satisfactory corrosionproofness in hydrochloric acid.

Optionally, the amorphous alloys set forth in claims 2 to 4 may incorporate therein Mo and/or W in a proportion of not more than 5 atomic % without jeopardizing the objects of the present invention.

The amorphous alloy of this invention having the quality described above is desirably produced by the sputtering technique.

The amorphous alloy-coated fabric of the present invention is produced by coating a substratal fabric with the Cu amorphous alloy by the sputtering technique.

The sputtering technique is one of the methods available for the production of an amorphous alloy. The production of an amorphous alloy the sputtering technique is carried out by the use of a target prepared by sintering or fusing a plurality of crystal phases having the same average composition as the amorphous alloy intended to be produced or by the use of a composite prepared by causing desired alloying elements to be embedded in a metallic plate made of main components of the amorphous alloy to be produced.

Specifically, this production is effected as follows.

It is difficult to prepare a Cu-Ta or Cu-Nb alloy target by the fusing technique. By the sputtering technique using a target prepared by embedding Ta and/or Nb in a Cu plate, the amorphous Cu-Ta, Cu-Nb, and Cu-Ta-Nb alloys enjoying high resistance to corrosion can be obtained. For the purpose of precluding the otherwise possible occurrence in the produced amorphous alloy of local heterogeneity of texture, it is desirable to have a plurality of substrates 12 to be revolved inside a sputtering device chamber around the axis of the chamber and have the substrates 12 themselves to be rotated as illustrated in Fig. 7 and Fig. 8 (wherein, the reference numeral 11 stands for the axis of the revolution of the substrates). Further, for the purpose of allowing the composition of the prospective amorphous alloy to be varied in a wide range, it is more advantageous to prepare two targets, i.e. one target 13 having either or both of Ta and Nb embedded in a Cu plate and the other target 14 using either Ta or Nb, and dispose these two targets in such a manner that they are mutually inclined and the substrate 12 is located near the intersection of the perpendiculars of these two targets as illustrated in Fig. 7 and effect simultaneous operation of the two targets while controlling their outputs severally with two power sources rather than to use one target 15 as illustrated in Fig. 8.

In accordance with this method, amorphous alloys of compositions conforming to the present invention are obtained by freely varying the concentrations of alloying elements in prospective amorphous alloys, using targets having Ti and Zr embedded Cu plates in addition to Ta and Nb, or varying combinations between targets and techniques. In the method using two targets, particularly the revolution and rotation of the plurality of substrates are necessary for the production of a homogeneous amorphous alloy.

The alloy of the composition conforming to this invention which is produced by the sputtering technique and the amorphous alloy layer in the coated fabric are both a single-phase amorphous alloy having the aforementioned elements homogeneously combined in the form of a solid solution. The amorphous alloy of this invention which is a homogeneous solid solution forms a protective film which enjoys extreme homogeneity and warrants a preeminent antibacterial property and high resistance to oxidation, discoloration, and corrosion.

The fabrics which are effectively usable in the present invention for the production of a Cu amorphous alloy-coated fabric include non-woven and woven fabrics of nylon, polyester, and polyurethane, for example.

The antibacterial amorphous alloy resistant to oxidation, discoloration, and corrosion contemplated by the present invention exhibits outstanding resistance to various fungi and bacteria and harmful organisms including (1) dermatomycosis, (2) staphylococci, (3) Escherichia coli, and (4) marine organisms (barnacles) and excels in resistance to oxidation and corrosion. Thus, it can be used very effectively as 1) an antibacterial deodorant material for insoles, 2) a material for precluding deposition of marine organisms, 3) a disinfectant wrapping material for foodstuffs, and 4) a deodorizing material for clothing, for example.

Now, the use of the amorphous alloy-coated fabric of this invention for the production of insoles contemplated by this invention will be described below with reference to the accompanying drawings.

Fig. 9 is a perspective view illustrating one example of the insole using an amorphous alloy-coated fabric of this invention and Fig. 10 and Fig. 11 are magnified cross sections taken through Fig. 9 along the line X-X.

An insole 21 in the present embodiment is constructed by superposing a gas-pervious layer 22 of polyvinylidene chloride (hereinafter occasionally referred to briefly as "layer"), a non-woven fabric 24 possessed of a coating layer 23 of Cu amorphous alloy, and a gas-pervious layer 25 of polyvinylidene chloride as reckoned from the surface (the surface to be touched by the user's foot) side.

The surface side polyvinylidene chloride layer 22 is intended to impart slipperiness to the insolve 21 so that the user's foot may be smoothly inserted into the shoe, prevent the insole from raising fluffs, and ensure the insole's retention of gas-perviousness. Generally, it is a woven fabric of polyvinylidene chloride fibers and has a thickness approximately in the range of from 0.1 to 3.0 mm.

The non-woven fabric 24 on which the coating layer 23 of Cu amorphous alloy is formed is intended to impart gas-perviousness and hygroscopicity to the insole 21. The non-woven fabric 24 has no particular restriction. Generally, it may be a non-woven fabric such as of nylon having a thickness approximately in the range of from 0.1 to 1.0 mm.

In order for the coating layer 23 of Cu amorphous alloy to retain the antibacterial property and the gas perviousness effectively, it is desired to have a thickness approximately in the range of from 100 Å to 1 μm.

The reverse side polyvinylidene chloride layer 25 of the insole 21 is intended to a cushioning property and gas perviousness. Generally, it has a honeycomb-like structure formed of polyvinylidene chloride in a thickness approximately in the range of from 0.1 to 3.0 mm.

The insole 21 of this description can be easily produced by interposing an amorphous alloy-coated fabric of this invention prepared by forming a coating layer 23 of Cu amorphous alloy on the non-woven fabric 24 between the polyvinylidene chloride layers 22, 25 and joining them fast as by the use of a welder.

Optionally , the rear side honeycomb-like polyvinylidene chloride layer 25 may be underlain by a gas-pervious layer 26 formed of a woven fabric of polyvinylidene chloride in a thickness approximately in the range of from 0.1 to 3.0 mm as illustrated in Fig. 11 so that the insole 21 may acquire enhanced water repellency.

The insole constructed as described above acquires outstanding antibacterial ability and deodorizing effect owing to the Cu ion present in the Cu amorphous alloy and retains these properties intact for a long time owing to the excellent corrosionproofness of the Cu amorphous alloy. In the amorphous alloy-coated fabric of this invention, since the coating layer of Cu amorphous alloy is formed by sputtering, it can be produced in a small thickness with high freedom of design and ample economy.

The insole illustrated in Figs. 9 to 11 is only one embodiment of the present invention. This invention need not be limited to this particular embodiment but may be practised otherwise without departing from the spirit of this invention. For example, what is obtained by forming the coating layer of Cu amorphous alloy on fibers destined to form a non-woven fabric and bonding the resultant coated fibers in the form of a non-woven fabric turns out to be a useful commodity.

As respect the antibacterial Cu amorphous alloy which is hihgly resistant to corrosion and useful for the insole of this invention, though the Cu amorphous alloys set forth in claims 1 to 4 are most desirable, such other amorphous alloys as Cu-Ta, Cu-Nb, Cu-Ta-Nb, Cu-Ta-Ti, Cu-Ta-Zr, Cu-Ta-Ti-Zr, Cu-Ta-Nb-Ti, Cu-Ta-Nb-Zr, and Cu-Tan-Nb-Ti-Zr are also usable.

The method to be adopted for the formation of the coating layer 3 of Cu amorphous alloy has no particular restriction. The method resorting to the sputtering operation, however, proves to be advantageous in that the sputtering is capable of forming a thin coating layer incapable of impairing the gas perviousness of the intermediate layer.

Owing to the use of Cu, an inexpensive substance, as an antibacterial component, the antibacterial amorphous alloy of this invention which is highly resistant to oxidation, discoloration, and corrosion and the amorphous alloy-coated fabric of this invention exhibit a conspicuous antibacterial action to various fungi, bacteria, and marine organisms and offer outstanding resistance to oxidation and corrosion and, therefore, retain the antibacterial property intact for a long time.

The antibacterial amorphous alloy of this invention which is highly resistant to oxidation, discoloration, and corrosion and the amorphous alloy-coated fabric of this invention are effectively usable in various forms in a wide variety of applications as for the protection of various daily commodities and building materials against propagation of contaminants and for the prevention of industrial facilities from deposition of marine organisms, for example. Thus, they enjoy very high economic utility.

Particularly, the amorphous alloy-coated fabric of this invention, when fabricated as an insole by being interposed between two opposed gas-pervious layers of polyvinylidene chloride, for example, can be used comfortably in all the seasons of the year because (1) the Cu ion manifests a high antibacterial deodorizing effect, (2) the amorphous texture of the Cu alloy excels in corrosionproofness and offers high resistance to oxidation and discoloration, (3) the antibacterial and deodorizing effect is retained intact for a long time, (4) the insole possesses a metallic gloss and excels in the warmth-retaining property, (5) the insole excels in hygroscopicity, gas perviousness, and a cushioning property, and (6) the insole can be constructed in a small thickness enough to avoid imparting any objectionable sensation to the wearer's foot and conform readily to the contour of the foot.

Further, the insole of the present invention possesses a highly desirable antibacterial deodorizing action, excels in corrosionproofness, precludes such adverse phenomena as deterioration, discoloration, and degeneration, and manifests the antibacterial deodorizing action for a long time.

Now, the present invention will be described more specifically below with reference to working examples. The numerals to be used hereinbelow in representing alloy compositions are expressed by the denomination of atomic percents.

Example 1:

A varying Cu-Ti-Ni-Ta amorphous alloy was tested for a polarizing property in 6N HCl kept at 30 ° C, to determine the relation between the Ta content of the alloy and the corrosionproofness. The results are shown in Fig. 5 and Fig. 6.

From Fig. 5 and Fig. 6, the following conclusions may be safely drawn.

The Cu-Ti alloy containing Ti, a metallic element famous for high corrosionproofness, is easily dissolved in 6N HCl. When this alloy incorporates Ta therein, the corrosionproofness thereof is notably improved in proportion as the Ta content thereof increases. When this amorphous alloy has a Ta content of not less than 15 atomic %, it is self-passivated to the extent of perfectly defying corrosion in a violently corrosive atmosphere. The corrosionproofness of the alloy of this kind is ascribable to the protective action generated by the passive film formed on the alloy surface. It has been demonstrated that in the passive film of an amorphous Cu alloy other than the Cu-34Ti cited in the working example, Ta and Ti which excel in corrosionproofness are concentrated to form a stable oxide and protect the matrix alloy and the amorphous alloy itself. It has been also demonstrated that the copper exists in the form of Cu^+ and this Cu^+ ion is preferentially dissolved in the solution.

Example 2:

Various amorphous alloys conforming to the present invention were tested for the antibacterial ability manifested on the following microbial strains by the method described hereinbelow. The results are shown in Table 2, Table 3, and Table 4.

Strains used for test

Trichophyton mentagrophtes IFO 6124
Staphylococcus aureus IFO 12732
Escherichia coli IFO 3301

Testing method

(1) Preparation of cell solution

A cell solution was prepared by culturing a test strain in an ordinary bouillon culture medium culture medium (35 ° C) and directly diluting the resultant culture broth with a sterilized phosphate buffer solution.

In the test with dermatomycosis, a cell solution prepared by culturing the test strain in a Sabouraud's agar culture medium incorporating therein 5% of blood for 14 days and suspending the cultured cells in an aqueous 0.05% polysorvate 80 solution was used.

(2) Test piece

Test pieces cut in the square of about 5 cm were used.

The materials subjected to the test were obtained by coating non-woven fabrics of nylon with alloys, a to D shown below, in a thickness of 500 Å. The materials for comparison were obtained by coating non-woven fabrics of nylon with alloys, E and F shown below, in the same thickness. An uncoated non-woven fabric of nylon was also used for the purpose of comparison.
Amorphous alloy A = Cu-65Ti-5Ta
Amorphous alloy B = Cu-50Ta
Amorphous alloy C = Cu-34Ta
Amorphous alloy D = Cu-15Ti-5Ta
Material for comparison E = Cu 100%
Material for comparison F = Stainless steel
Material for comparison G = Uncoated material

(3) Procedure of test

On a given test piece, a given cell solution was dropped until the test piece was amply impregnated with the cell solution. Then, the impregnated test piece was left standing at 25 ° C. After 6 hours' and 24 hours' standing, the test piece was examined to find respective numbers of live cells.

(4) Measurement of cell number

The test piece at the end of the standing was washed with a SCDLP liquid culture medium. The washings were subjected to the pour-plate culture treatment (35 ° C, two days) using a standard agar culture medium. The culture plate was examined to take count of live cells. The number of live cells per test piece was calculated based on the count.

In the test with dermatomycosis, the test piece was washed with a GPLP liquid culture medium. The washings were subjected to the pour-plate culture treatment (25 ° C, 14 days) using a potato dextrose agar culture medium. The culture plate was examined to take count of live cells. The number of live cells per test piece was calculated based on the count.

Table 2

Results of test for antibacterial property regarding dertomycosis					
Test piece		Cu content (atomic %)	Number of live cells (pieces/ml)		
			0	After 6 hours	After 24 hours
Amorphous alloy (examples of this invention)	A	30	$2.0x10^3$	0	0
	B	50	$3.6x10^5$	0	0
	C	66	$3.6x10^5$	0	0
	D	80	$2.0x10^3$	30	10
Materials for comparison	E	100	$3.6x10^5$	0	0
	F	Stainless steel	$3.6x10^5$	$3.0x10^5$	$2.0x10^5$
	G	Uncoated fabric	$3.6x10^5$	$3.5x10^5$	$3.5x10^5$

Table 3

Results of test for antibacterial property regarding staphylococcus					
Test piece		Cu content (atomic %)	Number of live cells (pieces/ml)		
			0	After 6 hours	After 24 hours
Amorphous alloy (examples of this invention)	A	30	$1.2x10^4$	0	0
	B	50	$2.4x10^6$	0	0
	C	66	$2.4x10^6$	0	0
	D	80	$1.2x10^4$	$1.0x10^2$	0
Material for comparison	E	100	$2.4x10^6$	0	0
	F	Stainless steel	$2.4x10^6$	$1.5x10^5$	$5.0x10^4$
	G	Uncoated fabric	$2.4x10^6$	$2.0x10^5$	$1.0x10^5$

Table 4

Results of test for antibacterial property regarding Escherichia coli					
Test piece		Cu content (atomic %)	Number of live cells (pieces/ml)		
			0	After 6 hours	After 24 hours
Amorphous alloy (examples of this invention)	A	30	$1.0x10^4$	0	0
	B	50	$1.0x10^4$	0	0
	C	66	$1.0x10^4$	0	0
	D	80	$1.0x10^4$	0	0
Material for comparison	E	100	$1.0x10^4$	0	0
	F	Stainless steel	$1.0x10^4$	$6.1x10^2$	35
	G	Uncoated fabric	$1.0x10^4$	$4.0x10^3$	$2.0x10^3$

It is clearly noted from Tables 2 to 4 that on the fabrics coated with Cu-amorphous alloys of the present invention, the numbers of live cells invariably of dermatomycosis responsible for athlete's foot, staphylococcus responsible for objectionable odor from filthy foot, and Escherichia coli decreased to 1/100 to 1/1,000 after six and decreased substantially to 0 after 24 hours, indicating that they yielded a conspicuous antibacterial effect as compared with the uncoated non-woven fabric. Particularly from Table 4, it is clear that the amorphous alloy-coated fabrics of this invention manifested a high antibacterial effect on Escherichia coli, one of the microbes generally accepted as responsible for food poisoning, as well as on dermatomycosis and staphylococcus.

In contrast, though the Cu in the material E for comparison manifested the same degree of antibacterial effect as the Cu amorphous alloy, the coating was appreciably dissolved by the time the test was completed. The stainless steel in the material for comparison F manifested a weak antibacterial effect.

Example 3:

A non-woven fabric (nylon) coated with a Cu-40Ti-10Ta amorphous alloy (in a thickness of 500 Å) and a non-woven fabric (nylon) coated with Cu (in the same thickness) were exposed to a varying test circomstances indicated in Table 5 for a varying test period also indicated in Table 5 and then examined as to the state of surface. The results are shown in Table 5.

It is clear from Table 5 that the amorphous alloys and amorphous alloy-coated fabrics conforming to the present invention were excellent in corrosionproofness, resistance to oxidation, and resistance to discoloration.

Table 5

Test circumstance (test period)	Amorphous alloy-caoted non-woven fabric	Cu-coated non-woven fabric (for comparison)
Immersion in water (7 days)	No discoloration (silver white color)	Discernible discoloration
Immersion in physiological saline salution (7 days)	No discoloration (silver white color)	Discernible discoloration
Exposure to outdoor conditions (7 days)	No discoloration (silver white color)	Discernible discoloration
Immersion in 1N hydrochloric acid (45 days)	No discoloration (silver white color)	Dissolution

Example 4:

The test pieces, H to K, indicated below were tied as arranged serially, to a wire of stainless steel and kept immersed in seawater along Ichihara pier facing Tokyo Bay during a summer period of 49 days from July 18 through September 4 to investigate adhesion of marine organisms. The surfaces of the test pieces removed from the seawater were visually examined. The results are shown in Table 6.

Test piece

H: Amorphous alloy (Cu-40Ti-10Ta)-coated non-woven fabric (nylon) (thickness of coating 500 Å)
I: Stainless steel pipe
J: Slate material
K: Uncoated non-woven fabric

It is clear from Table 6 that the amorphous alloys and amorphous alloy-coated fabrics conforming to the present invention were conspicuously effective in preventing adhesion of marine organisms.

Table 6

Test piece	Test results
H (example of this invention)	Only slight adhesion of marine organisms recognized. The entire surface of non-woven fabric retained metallic gloss.
I (comparison)	Adhesion of barnacles to the entire surface recognized.
J (comparison)	Adhesion of barnacles to the entire surface recognized.
K (comparison)	Adhesion of barnacles to the entire surface recognized.

Example 5:

Insoles of the construction illustrated in Fig. 9 to Fig. 11 were manufactured and subjected to a monitor test.

The components of insole were as follows.
Polyvinylidene chloride layer (woven fabric) 22, 0.8 mm in thickness
Cu amorphous alloy coating layer 23, 500 Å in thickness
Cu amorphous alloy composition: Cu-40Ti-10Ta
Non-woven fabric of nylon 24, 0.2 mm in thickness
Polyvinylidene chloride layer (honeycomb in construction) 25, 2.0 mm in thickness

In the monitor test, 150 monitors were asked to try the insoles for a period of about one month. Virtually all the monitors reported that the insoles were effective in eliminating objectionable odor of foot. Virtually all the monitors found the insoles to be resistant to dermatomycosis.

Claims

1. An antibacterial amorphous alloy highly resistant to oxidation, discoloration, and corrosion, comprising not less than 5 atomic % of Ta and/or not less than 15 atomic % of Nb, and Ti and Ni, and the balance substantially of Cu, characterized by the fact that the total content of Ta and/or Nb and Ti is in the range of from 30 to 62.5 atomic %, the content of Ni is in the range of from 0.6 to 4 times the content of Ta and/or Nb, and the content of Cu is in the range of from 0.6 to 4 times the content of Ti.

2. An antibacterial amorphous alloy highly resistant to oxidation, discoloration, and corrosion, comprising from 15 to 85 atomic % of Ta and/or Nb and the balance substantially of Cu.

3. An antibacterial amorphous alloy highly resistant to oxidation, discoloration, and corrosion, comprising not less than 1 atomic % of Ta, Ti and/or Zn and the balance substantially of Cu and characterized by the fact that the total content of Ta and Ti and/or Zr is in the range of from 15 to 85 atomic %.

4. An antibacterial amorphous alloy highly resistant to oxidation, discoloration, and corrosion, comprising a total of not less than 1 atomic % of Ta and Nb, Ti and/or Zr, and the balance substantially of Cu and

characterized by the fact that the total content of Ta and Nb and Ti and/or Zr is in the range of from 15 to 85 atomic %.

5. An alloy according to claim 1, wherein the Cu content is in the range of from 30 to 80 atomic % and the Ta content in the range of from 10 to 20 atomic %.

6. An alloy according to claim 2, wherein the Cu content is in the range of from 30 to 80 atomic % and the Ta content in the range of from 10 to 20 atomic %.

7. An alloy according to claim 3, wherein the Cu content is in the range of from 30 to 80 atomic % and the Ta content in the range of from 10 to 20 atomic %.

8. An alloy according to claim 4, wherein the Cu content is in the range of from 30 to 80 atomic % and the Ta content in the range of from 10 to 20 atomic %.

9. A method for the prevention of growth of a microorganism by the use of the alloy of claim 1 at the site of propagation of said microorganism.

10. A method for the prevention of growth of a microorganism by the use of the alloy of claim 2 at the site of propagation of said microorganism.

11. A method for the prevention of growth of a microorganism by the use of the alloy of claim 3 at the site of propagation of said microorganism.

12. A method for the prevention of growth of a microorganism by the use of the alloy of claim 4 at the site of propagation of said microorganism.

13. An amorphous alloy-coated fabric, produced by coating a substratal fabric by sputtering with an antibacterial amorphous alloy highly resistant to oxidation, discoloration, and corrosion, comprising not less than 5 atomic % of Ta and/or not less than 15 atomic % of Nb, and Ti and Ni, and the balance substantially of Cu, characterized by the fact that the total content of Ta and/or Nb and Ti is in the range of from 30 to 62.5 atomic %, the content of Ni is in the range of from 0.6 to 4 times the content of Ta and/or Nb, and the content of Cu is in the range of from 0.6 to 4 times the content of Ti.

14. An amorphous alloy-coated fabric, characterized by the fact that the coating is formed by sputtering an amorphous alloy comprising from 15 to 85 atomic 5 of Ta and/or Nb and the balance substantially of Cu.

15. An amorphous alloy-coated fabric, characterized by the fact that the coating is formed by sputtering an amorphous alloy comprising not less than 1 atomic % of Ta, Ti and/or Zr, and the balance substantially of Cu and characterized by the fact that the total content of Ta and Ti and/or Zr is in the range of from 15 to 85 atomic %.

16. An amorphous alloy-coated fabric, characterized by the fact that the coating is formed by sputtering an amorphous alloy comprising a total of not less than 1 atomic % of Ta and Nb, Ti and/or Zr, and the balance substantially of Cu and characterized by the fact that the total content of Ta and Nb and Ti and/or Zr is in the range of from 15 to 85 atomic %.

17. An insole having a copper-containing amorphous alloy-coated non-woven fabric interposed between gas-pervious layers of polyvinylidene chloride.

18. An insole according to claim 17, wherein said comprises not less than 5 atomic % of Ta and/or not less than 15 atomic % of Nb, and Ti and Ni, and the balance substantially of Cu and is characterized by the fact that the total content of Ta and/or Nb and Ti is in the range of from 30 to 62.5 atomic %, the content of Ni is in the range of from 0.6 to 4 times the content of Ta and/or Nb, and the content of Cu is in the range of from 0.6 to 4 times the content of Ti.

19. An insole according to claim 17, wherein said amorphous alloy comprises from 15 to 85 atomic % of

Ta and/or Nb and the balance substantially of Cu.

20. An insole according to claim 17, wherein said amorphous alloy comprises not less than 1 atomic % of Ta, Ti and/or Zr and the balance substantially of Cu and is characterized by the fact that the total content of Ta and Ti and/or Zr is in the range of from 15 to 85 atomic %.

21. An insole according to claim 17, wherein said amorphous alloy comprises a total of 1 atomic % of Ta and Nb, Ti and/or Zr and the balance substantially of Cu and is characterized by the fact that the total content of Ta and Nb and Ti and/or Zr is in the range of from 15 to 85 atomic %.

22. An insole according to claim 17, wherein said amorphous alloy is applied to said non-woven fabric by sputtering.

23. An insole according to claim 17, wherein the gas-pervious layer on the side for contact with the wearer's foot is made of an woven fabric of polyvinylidene chloride from 0.1 to 1.0 mm in thickness.

24. An insole according to claim 17, wherein said non-woven fabric is made of nylon.

25. An insole according to claim 17, wherein said non-woven fabric has a thickness in the range of from 0.1 to 1.0 mm.

26. An insole according to claim 17, wherein the gas-pervious layer on the side in contact with the inner bottom of shoe is a honeycomb layer of polyvinylidene chloride having a thickness in the range of from 0.1 to 3.0 mm.

27. An insole according to claim 17, wherein the coating layer of said amorphous alloy has a thickness in the range of from 100 Å to 1 µm.

FIG.1

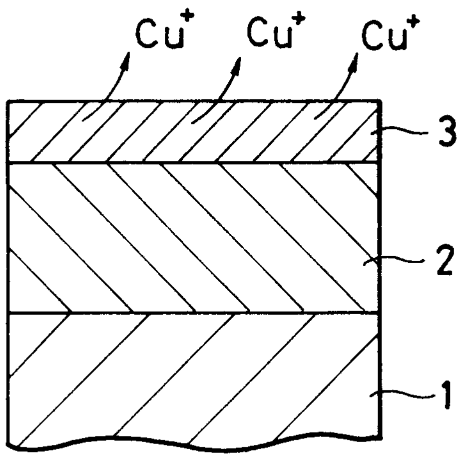


FIG.2

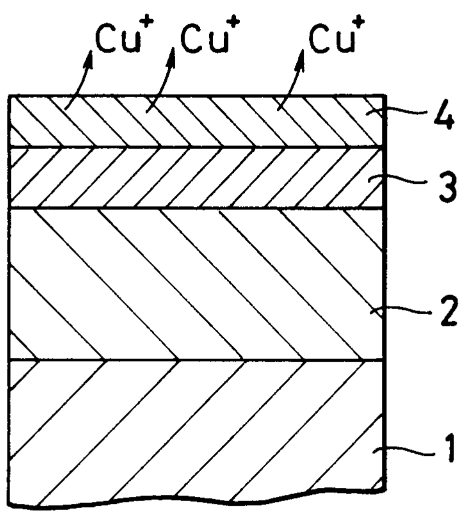


FIG.3

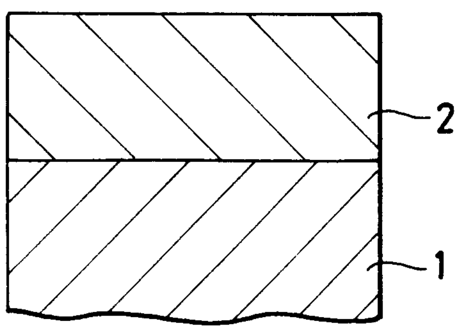


FIG.4

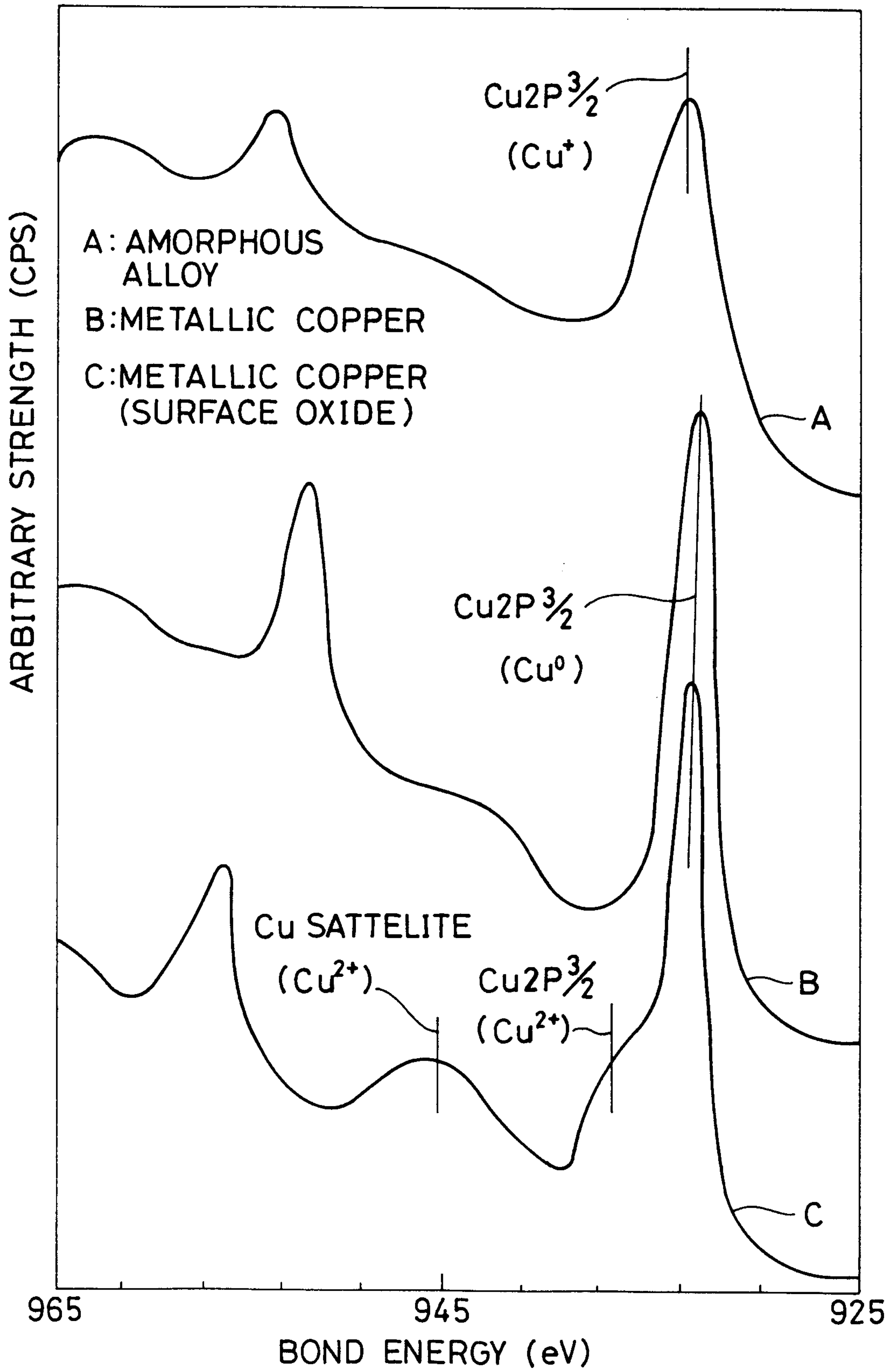

Cu2P3/2
(Cu+)
A: AMORPHOUS ALLOY
B:METALLIC COPPER
C:METALLIC COPPER (SURFACE OXIDE)
A
Cu2P3/2
(Cu0)
Cu SATTELITE
(Cu2+)
Cu2P3/2
(Cu2+)
B
C
ARBITRARY STRENGTH (CPS)
965
945
925
BOND ENERGY (eV)

FIG. 5

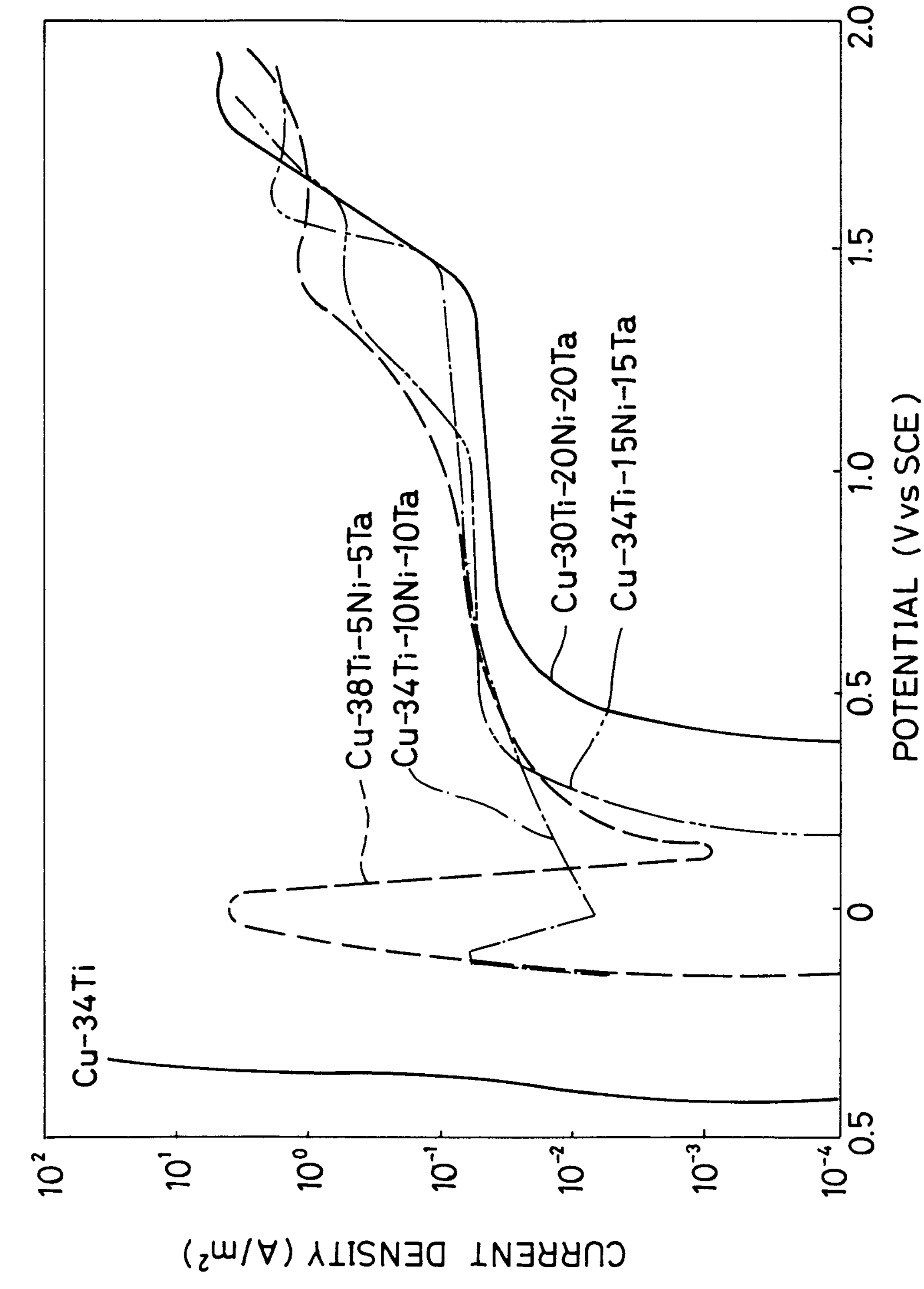

CURRENT DENSITY (A/m²)
POTENTIAL (V vs SCE)
Cu-34Ti
Cu-38Ti-5Ni-5Ta
Cu-34Ti-10Ni-10Ta
Cu-30Ti-20Ni-20Ta
Cu-34Ti-15Ni-15Ta
10²
10¹
10⁰
10⁻¹
10⁻²
10⁻³
10⁻⁴
-0.5
0
0.5
1.0
1.5
2.0

FIG.6

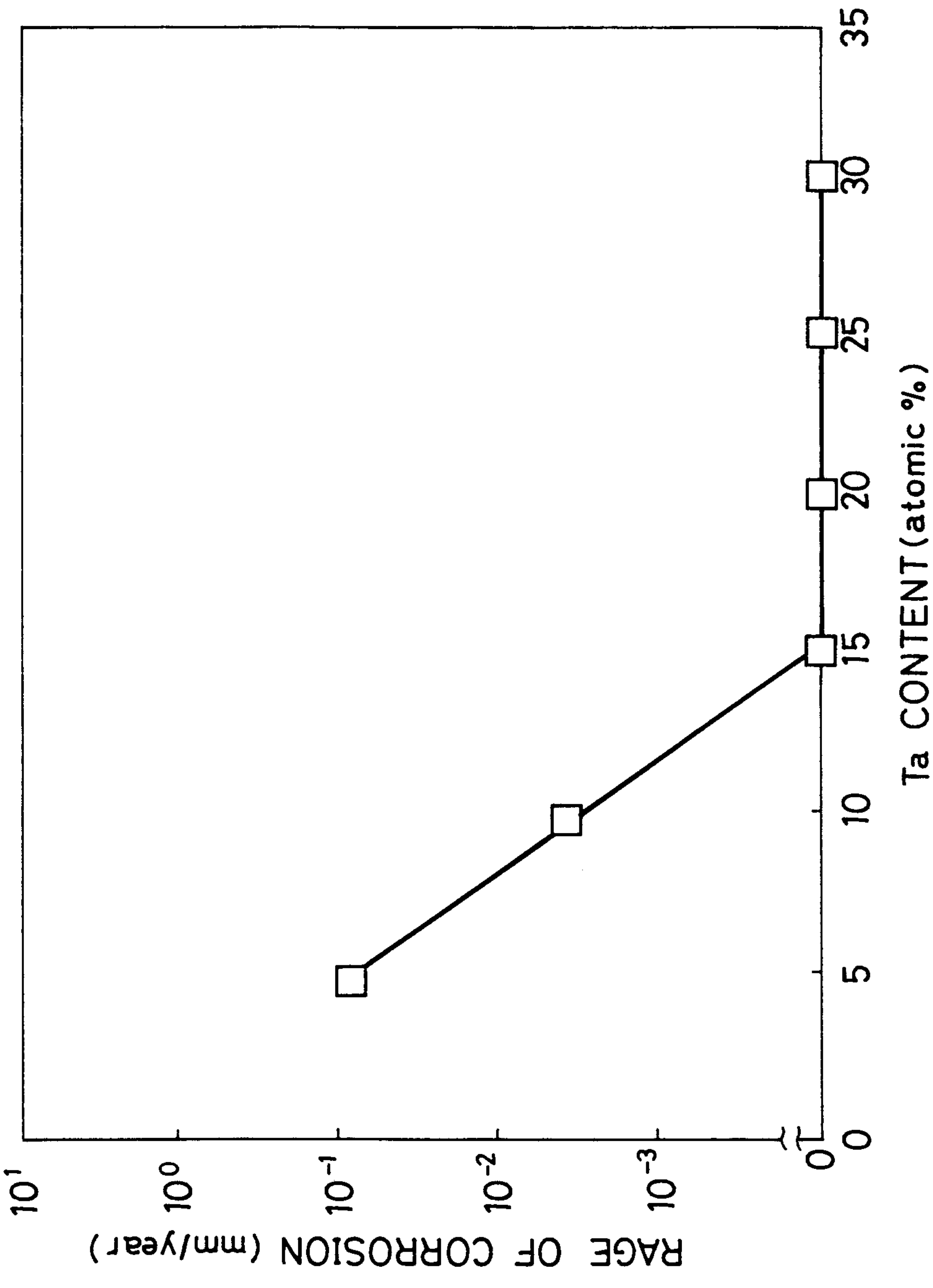

RAGE OF CORROSION (mm/year)
10^1
10^0
10^-1
10^-2
10^-3
0
Ta CONTENT (atomic %)
0
5
10
15
20
25
30
35

FIG.7

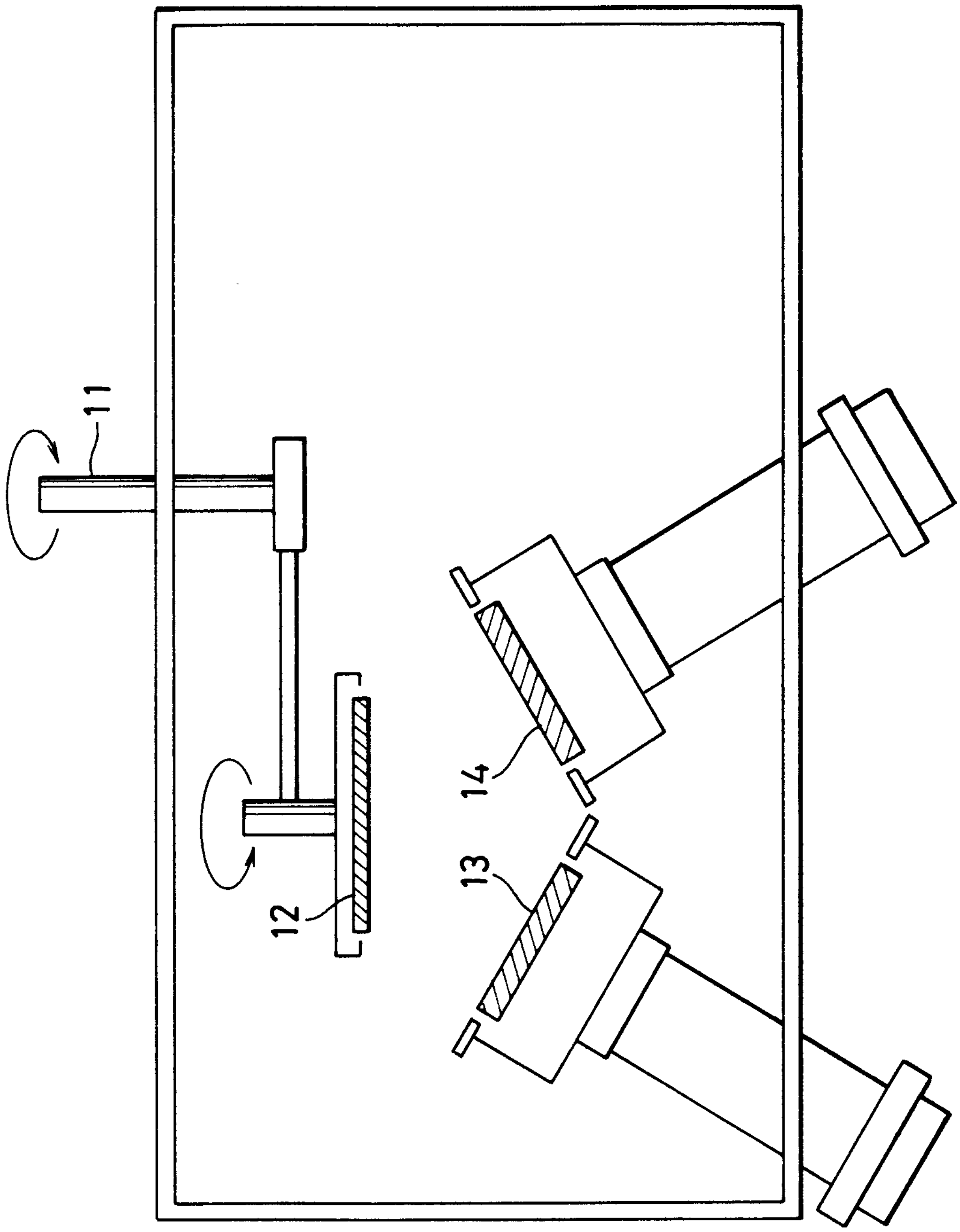


FIG.8

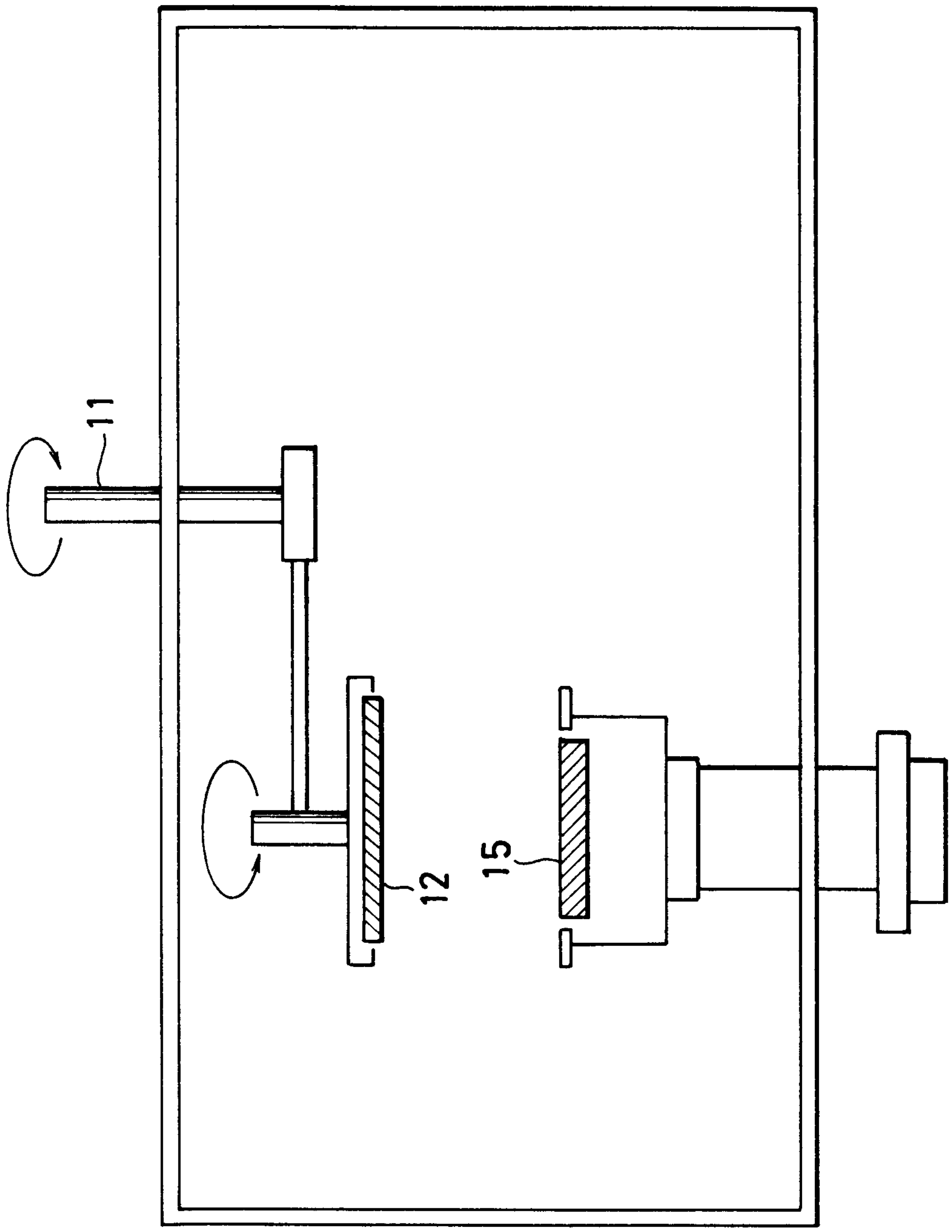


FIG.9

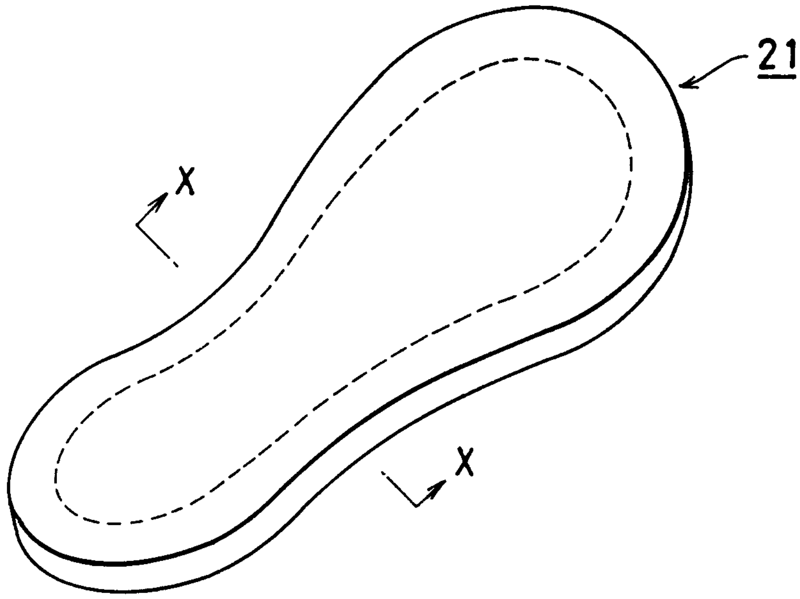


FIG.10

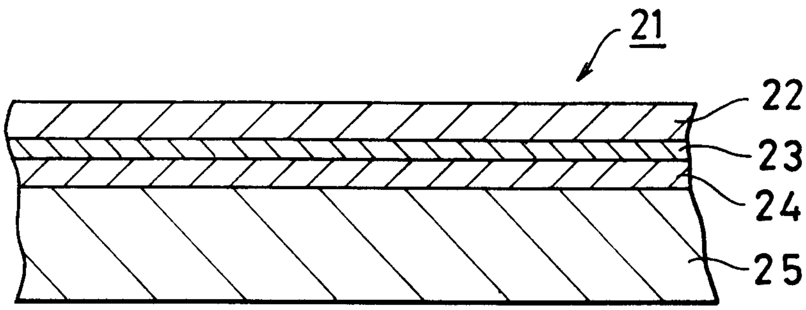
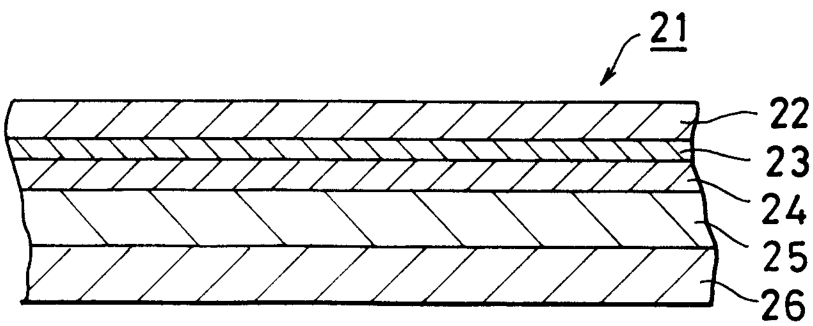


FIG.11



European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 11 9540

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X Y	EP-A-0 261 670 (MITSUI ENBINEERING & SHIPBUILDING CO.) *Claim; page 6, l.46-49; page 7, Table 2* ---	1-8 9-12, 17-21	C22C1/00 A43B17/04
X	DE-A-3 814 444 (MITSUI ENGINEERING & SHIPBUILDING CO.) *Claims 1-3; page 6, "Tabelle 2"; Figures 1 and 2* ---	1-8	
Y	US-A-5 001 848 (OKAYASU) *Claim 1; column 2, l.41-52 and l.60-68* ---	9-12, 17-21	
Y	GB-A-1 544 294 (TAKIZAWA) * the whole document * ---	9-12, 17-21	
A	US-A-4 206 514 (YAMAUCHI) * the whole document * ---	17,24	
A	GB-A-2 066 048 (CANE) -----		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C22C
A43B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	15 JULY 1992	LIPPENS M.H.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document