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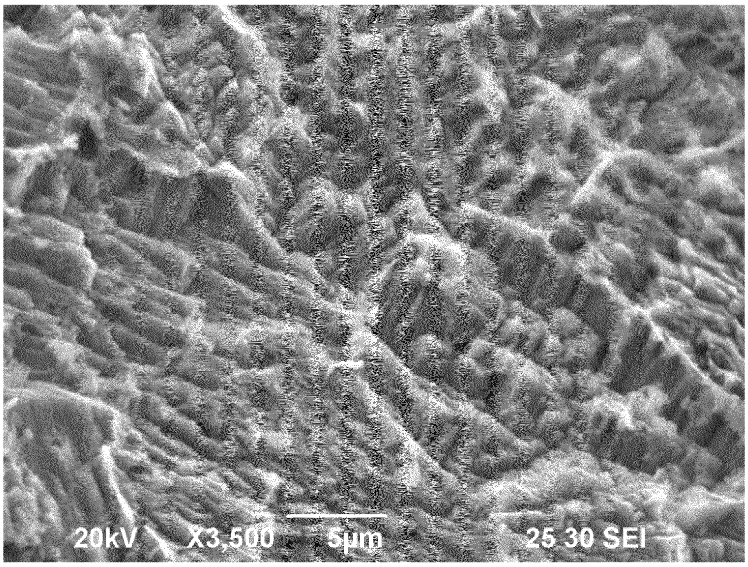
(54) ETCHING AGENT AND REPLENISHING LIQUID

(57) Disclosed is an etching agent for steel. The etching agent is an acidic aqueous solution including ferrous ions, ferric ions, and an acetylene group-containing water-soluble compound. The concentration of ferrous ion A% by weight and the concentration of ferric ion B% by weight in the etching agent is preferably from 0.1 to 2.5. Also disclosed is a replenishing liquid that is added to the etching agent when the etching agent is continuously or repeatedly used. The replenishing liquid is an aqueous solution including an acetylene group-containing water-soluble compound.

FIG. 2



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Description

TECHNICAL FIELD

[0001] The invention relates to an etching agent for steel and a replenishing solution for the etching agent.

BACKGROUND ART

[0002] A technology for bonding steel material and resin or other materials into a composite has been developed in various industrial fields, mainly in the field of automobiles. For example, Patent Document 1 listed below proposes a method for improving the adhesion between steel material and fiber-reinforced plastic or other materials, which includes etching steel material with an aqueous solution of a non-oxidative strong acid to roughen the steel material and then bonding the steel material to the target material.

PRIOR ART DOCUMENT

PATENT DOCUMENT

[0003] Patent Document 1: WO 2008/146833 A

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0004] However, the inventors' study has revealed that the roughening of steel material with an aqueous solution of a non-oxidative strong acid according to Patent Document 1 still remains insufficient for improving the adhesion between steel material and the target material.

[0005] The invention, which has been accomplished in view of the above problem with the conventional art, provides an etching agent for steel that is capable of allowing steel materials to have improved adhesion to target materials, and also provides a replenishing solution for such an etching agent.

MEANS FOR SOLVING THE PROBLEMS

[0006] The etching agent of the invention is an etching agent for steel that is an acidic aqueous solution including ferrous ions, ferric ions, and an acetylene group-containing water-soluble compound. The etching agent has a ratio of ferrous ion content to ferric ion content in a specific range.

[0007] The replenishing solution of the invention is a replenishing solution that is to be added to the etching agent of the invention for continuous or repeated use of the etching agent. The replenishing solution is an aqueous solution containing an acetylene group-containing water-soluble compound.

EFFECTS OF THE INVENTION

[0008] When a steel material is etched with the etching agent of the invention, fine irregularities with shapes suitable for adhesion to target materials are uniformly formed on the surface of the steel material. Steel material treated with the etching agent of the invention have high adhesion to resins or other target materials.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009]

FIG. 1 is a perspective view showing the structure of a sample for tensile shear strength measurement.
FIG. 2 is a scanning electron micrograph of an SPCC surface roughened with an etching agent of an example.
FIG. 3 is a scanning electron micrograph of an SPCC surface roughened with an etching agent of a comparative example.
FIG. 4 is a scanning electron micrograph of an SPCC surface before an etching treatment.

MODE FOR CARRYING OUT THE INVENTION

<Etching agent>

[0010] The etching agent for the steel according to the invention is an acidic aqueous solution including ferrous ions, ferric ions, and an acetylene group-containing water-soluble compound. Hereinafter, each component in the etching agent of the invention will be described.

(Ferric ion)

[0011] Ferric ion is a component capable of oxidizing steel. Adding a ferric ion source allows the etching agent to contain ferric ions. Examples of the ferric ion source include, but are not limited to, ferric sulfate, ferric chloride, ferric nitrate, ferric hydroxide, and ammonium iron(III) sulfate. These may be used alone or in combination of two or more. Among the ferric ion sources, ferric sulfate, ferric hydroxide, and ammonium iron(III) sulfate are preferred in order to maintain the etching rate at a proper level.

(Ferrous ion)

[0012] The etching agent of the invention contains ferrous ions. When the etching agent contains ferrous ions in addition to ferric ions, fine irregularities can be formed on the surface of steel material. Adding a ferrous ion source allows the etching agent to contain ferrous ions. Examples of the ferrous ion source include, but are not limited to, ferrous sulfate, ferrous chloride, ferrous nitrate, ferrous hydroxide, and ammonium iron(II) sulfate. These may be used alone or in combination of two or more. Among the ferrous ion sources, ferrous sulfate, ferrous hydroxide, and ammonium iron(II) sulfate are preferred in order to form fine irregularities suitable for improvement of adhesion and to reduce costs.

(Acetylene group-containing water-soluble compound)

[0013] The acetylene group-containing water-soluble compound is a component added for forming fine irregularities uniformly on the surface of steel material. The acetylene group-containing water-soluble compound may be any compound that has an acetylene group and is soluble in an amount of 0.01% by weight or more in water. For example, a compound having an acetylene group and a hydrophilic group may be used as the acetylene group-containing water-soluble compound. The hydrophilic group may be, for example, a hydroxy group, an amino group, a carboxyl group, or a quaternary ammonium group. In particular, a compound having an acetylene group and a hydroxy group is preferred for forming fine irregularities uniformly on the surface of steel material. The acetylene group-containing water-soluble compound may also have a hydroxy group as part of a carboxylic acid (in other words, hydroxy group-containing compounds are intended to also include carboxyl group-containing compounds). The acetylene group-containing water-soluble compound may also be a diyne or triyne compound having two or more acetylene groups per molecule and may also have two or more hydroxy groups per molecule.

[0014] The compound having an acetylene group and an amino group may be, for example, propargylamine or N,N-diethyl-1-propyn-1-amine. The compound having an acetylene group and a quaternary ammonium group may be, for example, N,N,N-trimethyl-2-propyn-l-aminium. Examples of the compound having an acetylene group and a hydroxy group include compounds having one acetylene group and one hydroxy group, such as 2-butyn-1-ol, 2-pentyn-1-ol, 3-pentyn-1-ol, 3-hexyn-1-ol, 2-hexyn-1-ol, 3-heptyn-1-ol, 4-heptyn-2-ol, 2-heptyn-1-ol, 5-heptyn-3-ol, 3-octyn-1-ol, 3-phenyl-2-propyn-1-ol, 3-nonyn-1-ol, 2-decyn-1-ol, 3,5-dimethyl-1-hexyn-3-ol, 3-decyn-1-ol, 4-diethylamino-2-butyn-1-ol, and 4-(3-aminophenyl)-2-methyl-3-butyn-2-ol; compounds having two acetylene groups and one hydroxy group, such as 2,2,8,8-tetramethyl-3,6-nonadiyn-5-ol, 4,6-nonadecadiyn-1-ol, and 10,12-pentacosadiyn-1-ol; compounds having one acetylene group and two hydroxy groups, such as 2-butyne-1,4-diol, 3-hexyne-2,5-diol, 2,5-dimethyl-3-hexyne-2,5-diol, 3,6-dimethyl-4-octyne-3,6-diol, 1,4-bis(2-hydroxyethoxy)-2-butyne, 2,4,7,9-tetramethyl-5-decyne-4,7-diol, 2,4,7,9-tetramethyl-5-decyne-4,7-diol, 3,6-dimethyl-4-octyne-3,6-diol, 3,6-dimethyl-4-octyne-3,6-diol, and 5-phenyl-4-pentyn-1-ol; compounds having one acetylene group and two hydroxy groups, such as 2,4-hexadiyne-1,6-diol; compounds having one acetylene group and one carboxyl group, such as 2-butynoic acid, 2-hexynoic acid, 2-heptynoic acid, and phenylpropiolic acid; compounds having one acetylene group and two carboxyl groups, such as acetylenedicarboxylic acid, and salts thereof (such as potassium acetylenedicarboxylate); and compounds having two acetylene groups and one carboxyl group, such as 2,4-pentadecadiynoic acid, 10,12-heptadecadiynoic acid, 2,4-nonadecadiynoic acid, 2,4-heneicosadiynoic acid, 10,12-tricosadiynoic acid, and 10,12-pentacosadiynoic acid. In the invention, a single acetylene group-containing water-soluble compound may be used, or two or more kinds of acetylene group-containing water-soluble compound may be used in combination.

(Acid component)

[0015] The etching agent of the invention is an acidic aqueous solution and thus contains an acid component. The acid component is a component capable of dissolving metals (mainly ferrous ions) which leach from steel when oxidized by ferric ions or other substances. Examples of the acid component include hydrohalic acids such as hydrofluoric acid, hydrochloric acid (muriatic acid), hydrobromic acid, and hydroiodic acid; sulfuric acid, nitric acid, phosphoric acid, perchloric acid, sulfamic acid, and other inorganic acids; or organic acids such as sulfonic acid and carboxylic acids. In the invention, these may be used alone or in combination of two or more. Among these acid components, inorganic acids are preferred in order to increase the acid concentration of the etching agent so that the etching rate can be maintained at an appropriate level. In particular, sulfuric acid, sulfamic acid, and sulfonic acid are preferred in order to uniformly form fine irregularities on the surface of steel material and to reduce costs.

(Concentration of each component)

[0016] As described above, the etching agent of the invention contains ferrous ions, ferric ions, an acetylene group-containing water-soluble compound, and an acid component. When the concentration of each of these components is set in a specific range, fine irregularities with characteristic shapes can be uniformly formed on the surface of steel material.

[0017] In the etching agent of the invention, a ratio A/B between ferrous ion concentration A% by weight and a ferric ion concentration B% by weight is preferably from 0.1 to 2.5, more preferably from 0.15 to 2.0, further preferably from 0.2 to 1.5. When the concentration ratio A/B of the ferrous ions to the ferric ions is set in the above range, fine irregularities can be formed on the surface of steel material.

[0018] The ferric ion concentration in the etching agent of the invention is preferably from 0.2 to 20% by weight, more preferably from 0.5 to 15% by weight, further preferably from 1.0 to 10% by weight. When the ferric ion concentration is 0.2% by weight or more, the etching rate can be maintained at a proper level. On the other hand, when the ferric ion concentration is 20% by weight or less, the ferric ions can remain soluble and stable in the etching agent, and the etching amount can be easily controlled.

[0019] The ferrous ion concentration is preferably from 0.02 to 5% by weight, more preferably from 0.03 to 4% by weight, further preferably from 0.05 to 3% by weight. When the ferrous ion concentration is 0.01% by weight or more, fine irregularities suitable for improvement of adhesion can be easily formed. On the other hand, when the ferrous ion concentration is 5% by weight or less, the etching rate can be maintained at a proper level.

[0020] The concentration of the acetylene group-containing water-soluble compound is preferably from 0.01 to 5% by weight, more preferably from 0.02 to 2% by weight, further preferably from 0.05 to 1% by weight, in order to uniformly form fine irregularities on the surface of steel material. The ratio S/B between the concentration (S% by weight) of the acetylene group-containing water-soluble compound and the concentration (B% by weight) of the ferric ions is preferably from 0.001 to 100, more preferably from 0.01 to 10, further preferably from 0.07 to 5.

[0021] The concentration of the acid component is preferably such that the resulting hydrogen ion concentration is from 0.02 to 1.3% by weight, more preferably from 0.03 to 1.0% by weight, further preferably from 0.05 to 0.8% by weight. When the hydrogen ion concentration is 0.02% by weight or more, the etching rate (rate of dissolution) of steel material can be prevented from decreasing. On the other hand, when the hydrogen ion concentration is 1.3% by weight or less, precipitation of metal salt crystals can be prevented when the etching agent temperature decreases. In this case, workability can also be improved, and cost reduction can be easily achieved.

(Other components)

[0022] Other components may also be added to the etching agent of the invention as long as the effects of the invention are not impaired. Such other components may include, for example, surfactants, compounds capable of coordinating to metals (metal coordination compounds), and anti-foaming agents. In this regard, such other components differ from the acetylene group-containing water-soluble compound. Metal coordination compounds may include, for example, chelating agents such as carboxylic acid chelating agents, phosphonic acid chelating agents, and amine chelating agents, nitrogen-containing compounds, and sulfur-containing compounds. Metal coordination compounds can control the shape of irregularities on the surface of steel material by coordinating to metals on the surface of steel to suppress the leaching of metal ions from the surface of steel or contrarily by coordinating to metal ions leaching from the surface of steel to accelerate the leaching of metal ions. Therefore, when one or two or more metal coordination compounds are selected appropriately, the shape of irregularities on the surface of steel material can be controlled to be suitable for improvement of adhesion. When these components are added, their concentration is preferably from about 0.01 to about 10.0% by weight.

[0023] The etching agent of the invention can be easily prepared by dissolving each of the above components, for example, in ion-exchanged water or the like.

<Replenishing solution>

[0024] The replenishing solution of the invention is to be added to the etching agent of the invention for continuous or repeated use of the etching agent. The replenishing solution of the invention is an aqueous solution containing the acetylene group-containing water-soluble compound. By adding the replenishing solution to the etching agent, the proportion of each component in the etching agent can be maintained at a proper level, so that the above effects of the etching agent of the invention can be stably maintained.

[0025] The replenishing solution may be added to the etching agent of the invention in order to control the acid concentration of the etching agent or suppress fluctuations in the acid concentration. For this purpose, the replenishing solution is preferably an acidic aqueous solution. The replenishing solution of the invention may also contain ferrous ions, ferric ions, or other components capable of being added to the etching agent. Each component of the replenishing solution may be the same as that capable of being added to the etching agent of the invention.

[0026] The concentration of the acetylene group-containing water-soluble compound in the replenishing solution may be appropriately set depending on the concentration of the acetylene group-containing water-soluble compound in the etching agent. In order to maintain the above effects of the etching agent of the invention stably, the concentration of the acetylene group-containing water-soluble compound in the replenishing solution is preferably from about 0.01 to about 7.5% by weight.

<Method of using the etching agent>

[0027] Next, a description will be given of a preferred method of using the etching agent of the invention (hereinafter also referred to as the present use method). In the present use method, steel materials can be etched, such as carbon steel, high tensile strength steel, low temperature steel, reactor steel plates, and other steel materials. Specific examples of steel materials include cold-rolled steel products (Steel Plate Cold Commercial SPCC), hot-rolled steel products (Steel Plate Hot Commercial SPHC), structural automobile hot-rolled steel products (Steel Automobile Press Hot; SAPH), hot-rolled high-tensile-strength steel sheets for automobiles (Steel Plate Formability Hot; SPFH), general structural rolled steel products (SS materials) mainly for machining purposes, and other structural steel materials for bodies and parts of various machines. These many steel materials can be pressed or cut or undergo other processes. Therefore, the structure and shape of the steel materials may be freely selected. In the invention, the term "steel" or "steel material" is intended to include not only the steel materials mentioned above but also every type of steel or steel material standardized by Japanese Industrial Standards (JIS), International Organization for Standardization (ISO), or other standards. The present use method may be used to perform, for example, a process of removing a steel material by etching (inclusive of a process of removing only a part of the material) or a process of surface-treating a steel material. In particular, when a steel material is surface-treated (micro-etched) with the etching agent of the invention, fine irregularities with characteristic shapes can be uniformly formed on the surface of the steel material, so that the steel material can have significantly improved adhesion to target materials such as resins.

(Pretreatment)

[0028] The present use method may include subjecting the surface of a steel material to degreasing, mechanical polishing such as sand blasting, shot blasting, grinding, or mass finishing, chemical polishing, or other processes before treating the steel material with the etching agent of the invention.

(Etching treatment)

[0029] The method of treating the steel material with the etching agent of the invention may be, for example, a method of spraying the etching agent on the surface of the steel material to be treated, or a method of immersing the steel material in the etching agent to treat the steel material. In the spraying method, the etching is preferably performed under the conditions of an etching agent temperature of 20 to 40°C, a spray pressure of 0.05 to 0.3 MPa, and a period of 30 to 300 seconds. In the immersing method, the etching is preferably performed under the conditions of an etching agent temperature of 30 to 60°C and a period of 60 to 600 seconds.

[0030] When the surface of the steel material is treated with the etching agent, fine irregularities are uniformly formed on the surface of the steel material. The average etching amount (the average amount of dissolution) with the etching agent in the depth direction of the steel material is preferably from 0.5 to 10.0 μm, more preferably from 0.75 to 8.0 μm, further preferably from 1.0 to 5.0 μm, when calculated from the weight, specific gravity, and surface area of the dissolved steel material. When the etching amount is 0.5 μm or more, fine irregularities with shapes suitable for improvement of adhesion can be easily formed. When the etching amount is 10.0 μm or less, the treatment can be performed in a reduced time. The etching amount can be controlled by the treatment temperature, the treatment time, or other conditions.

[0031] In the present use method, the whole or part of the surface of the steel material may be treated with the etching agent. For example, when a composite of a steel material and a resin or other material is formed, a part of the surface of the steel material may be selectively treated with the etching agent, in which the part is to be bonded to the resin or other target material. In the present use method, the etching with the etching agent may be performed in combination with wet etching with any other etching agent or any of various types of dry etching as long as the effects of the invention are not impaired.

(Post-treatment)

[0032] After the treatment with the etching agent, the surface of the steel material is chemically active and has an increased surface area. Therefore, the surface of the steel material tends to quickly form an oxide film when coming into contact with air. In some cases, this oxide film can interfere with the adhesion between the steel material and the resin or other material. Therefore, acid cleaning is preferably performed as a post-treatment in order to remove the oxide film. The acid for use in this treatment may be of any type. When hydrochloric acid or nitric acid is used, the surface of the steel material can easily undergo re-oxidation. Therefore, the acid for use in the post-treatment is preferably selected from acids other than hydrochloric acid and nitric acid. In particular, a polybasic acid such as malic acid, malic acid, citric acid, or tartaric acid is preferably used in order to prevent re-oxidation.

[0033] After the acid cleaning, washing with water and drying are preferably performed. If chloride ions remain on the surface of the steel material, they will tend to promote re-oxidation. Therefore, ion-exchanged water is preferably used in the washing with water after the acid cleaning. Re-oxidation can also easily occur if water remains on the surface of the steel material after the washing with water. Therefore, drying is preferably performed with the application of sufficient heat after the washing with water.

[0034] The steel material having undergone the process to the drying in this way is preferably prevented from undergoing re-oxidation-induced reduction in bondability during the period until the steel material is bonded to a target material such as a resin. In order to prevent re-oxidation, the steel material after the etching treatment is preferably stored in a sealed state where water is blocked. Additionally, to prevent re-oxidation during the storage, a rust prevention treatment may also be performed on the steel material after the etching treatment. This treatment may be performed using any of a wide variety of water-soluble corrosion inhibitors commonly used, such as amines, phosphates, nitrites, chromates, and alkali metal salts of organic acids. It should be noted that if the rust prevention treatment is performed using a solvent-based corrosion inhibitor or an emulsion corrosion inhibitor, an oil film having a tendency to interfere with the adhesion to the target material can be formed on the surface of the steel material. A method of wrapping the steel material with anti-rust paper impregnated with a volatile corrosion inhibitor and storing the wrapped steel material may also be used instead of or in addition to the rust prevention treatment.

<Uses of the steel material after the treatment>

[0035] The steel material treated by the present use method can be used, for example, not only as a material for the steel-resin composite described below but also as a steel material having the ability to be wetted by various solvents. The steel material treated by the present use method is also expected to have effectively improved adhesion not only to resins but also to glass, plated metal coatings, inorganic semiconductors, organic semiconductors, ceramics, and other materials. The present use method may be used not only for a roughening process but also for a process of removing a steel material by etching (inclusive of a process of removing only a part of the material).

<Steel-resin composite>

[0036] Next, a description will be given of a steel-resin composite, which is obtained by bonding a steel material and a resin composition into one body, as an example of use of the steel material treated by the present use method. The steel-resin composite can be obtained by a process that includes treating a steel material by the present use method described above and then bonding a resin composition to the treated surface of the steel material. When the steel material is treated with the etching agent of the invention, irregularities suitable for improvement of adhesion between the steel material and a resin composition are uniformly formed on the surface of the steel material, so that the steel material can be bonded with improved adhesion to the resin composition. The method for bonding the resin composition to the surface of the steel material treated by the present use method may be, but not limited to, injection molding, extrusion molding, hot press molding, compression molding, transfer molding, cast molding, laser welding molding, reaction injection molding (RIM), LIM molding, or any other resin molding method. A composite of steel and a resin composition coating may also be produced by forming a resin composition coating on the surface of the steel material. In this case, a coating method may be used in which a solution or dispersion of the resin composition in a solvent is applied to the steel material, or various other methods of application may be used. Other methods of application include, for example, baking finish, electro-deposition coating, electrostatic coating, powder coating, and ultraviolet-curing coating. The molding methods listed above may be performed under known conditions selected depending on the resin composition.

[0037] The steel-resin composite may be produced using any resin composition capable of being bonded to the surface of the steel material by any of the molding methods listed above. The resin composition may be selected from thermoplastic resin compositions and thermosetting resin compositions depending on the intended use.

(Thermoplastic resin composition)

[0038] When a thermoplastic resin composition is used, the thermoplastic resin composition may include, as a main component, one or a combination of two or more of polyamide resin such as polyamide 6 or polyamide 66, polyethylene resin, polypropylene resin, acrylonitrile-styrene copolymer resin, acrylonitrile-butadiene-styrene copolymer resin, polyvinyl chloride resin, polycarbonate resin, polyacetal resin, polybutylene terephthalate resin, polyethylene terephthalate resin, polyethylene naphthalate resin, polyphenylene sulfide resin, liquid crystalline polyester resin, polyimide resin, syndiotactic polystyrene resin, polycyclohexane dimethylene terephthalate resin, fluororesin, polyvinyl acetate resin, modified polyphenylene ether resin, polyether sulfone resin, amorphous polyarylate resin, aromatic polyether ketone resin, ethylene-vinyl acetate copolymer resin, ethylene-acrylic acid copolymer resin, and ethylene-methacrylic acid resin.

[0039] A composition including any of the thermoplastic resins listed above may be used as the thermoplastic resin composition. As long as the effects of the invention are not impaired, the composition including any of the thermoplastic resins listed above may also contain any of additives conventionally known in the art, such as various inorganic and organic fillers, flame retardants, flame retardant aids, ultraviolet absorbers, thermal stabilizers, light stabilizers, colorants, carbon black, processing aids, nucleating agents, mold release agents, plasticizers, and fibrous reinforcing materials.

(Thermosetting resin composition)

[0040] When a thermosetting resin composition is used, the thermosetting resin composition may include, as a main component, one or a combination of two or more of phenolic resin, epoxy resin, urea resin, melamine resin, unsaturated polyester resin, polyimide resin, diallyl phthalate resin, alkyd resin, polyurethane resin, cyanate resin, and silicone resin.

[0041] A composition including any of the thermosetting resins listed above may be used as the thermosetting resin composition. As long as the effects of the invention are not impaired, the composition including any of the thermosetting resins listed above may also contain any of additives conventionally known in the art, such as various inorganic and organic fillers, flame retardants, flame retardant aids, ultraviolet absorbers, thermal stabilizers, light stabilizers, colorants, carbon black, processing aids, nucleating agents, mold release agents, plasticizers, and fibrous reinforcing materials.

(Other resin compositions)

[0042] Various other resin compositions may also be used, such as light-curing resin compositions containing acrylic resin, styrene resin, or the like, and reaction-curing resin compositions containing rubber, an elastomer, or the like.

[0043] The steel-resin composite is preferably used for the manufacture of electronic device components, home appliance components, transportation machine components, or various other machine components. More specifically, the steel-resin composite is suitable for use in various electronic device components including those for mobile applications, home appliance components, medical instrument components, vehicle structural components, and vehicle-mounted components.

EXAMPLES

[0044] Next, examples of the invention will be described together with comparative examples. It will be understood that the examples described below should not be construed to limit the invention.

<Treatment with etching agent>

[0045] Dull-finished, cold-rolled sheets with a width of 20 mm, a length of 30 mm, and a thickness of 2.3 mm (manufactured by NIPPON STEEL & SUMITOMO METAL CORPORATION) were provided as test substrates. The test substrates were subjected to a pretreatment in which they were immersed in acetone and degreased for 15 minutes with the application of ultrasonic waves. Each test substrate was then immersed in each etching agent shown in Tables 1 and 2 and etched at 50°C for an etching time that was so adjusted that iron could be etched in an amount of 2.0 μm. Tables 1 and 2 show the components of each etching agent, in which ion-exchanged water is the balance of the composition, and all % concentrations are by weight.

[0046] After the etching, the etched surface of each test substrate was immersed in a 5% tartaric acid solution at a temperature of 25°C for 15 seconds. Subsequently, each test substrate was washed with ion-exchanged water. Each test substrate was drained and then dried in an oven at 120°C for 10 minutes.

<Tensile shear strength measurement test>

[0047] As shown in FIG. 1, a sample for tensile shear strength measurement was prepared by placing an FRP sheet 3 (10 mm wide, 30 mm long, 1.6 mm thick) on the surface of the treated test substrate 1 with an epoxy-impregnated glass cloth prepreg 5 (product name: R-1661, manufactured by Panasonic Corporation, 5 mm x 10 mm x 0.1 mm thick) in between, temporarily fixing them with a heat-resistant polyimide tape, and then heating them in an oven at 160°C for 90 minutes to cure the prepreg.

[0048] The sample for measurement was clamped at its steel sheet and FRP parts when the tensile shear strength of its joint part was measured using an autograph (model number: AGS-X10kN manufactured by Shimadzu Corporation). Tables 1 and 2 show the results.

[Table 1]

	Formulation		H^+ (%)	Fe^{2+} (%)	Fe^{3+} (%)	A/B	Etching rate (μm/minute)	Tensile shear strength (MPa)
Example 1	Sulfuric acid (62.5%)	39.20%	0.50	0.20	0.20	1.00	0.69	31.9
	Iron(II) hydroxide	0.03%						
	Ammonium iron(III) sulfate dodecahydrate	1.73%						
	2,4-hexadiyne-1,6-diol	0.50%						
Example 2	Acetic acid (90%)	13.34%	0.20	5.00	2.00	2.50	2.16	35.7
	Iron(II) acetate	15.57%						
	Iron(III) sulfate pentahydrate	8.77%						
	4,6-Nonadecadiyn-1-ol	1.00%						
Example 3	Methanesulfonic acid	9.61%	0.10	2.00	20.00	0.10	7.38	28.4
	Iron(II) chloride tetrahydrate	7.12%						
	Iron(III) chloride	58.10%						
	10,12-Pentacosadiynoic acid	1.00%						
Example 4	Phosphoric acid (89%)	29.36%	0.80	0.50	0.20	2.50	0.82	34
	Iron(II) sulfate heptahydrate	2.49%						
	Iron(III) hydroxide	0.32%						
	2,5-Dimethyl-3-hexyne-2,5-diol	0.10%						
Example 5	Sulfuric acid (98%)	65.00%	1.30	1.00	1.00	1.00	1.47	38.8
	Iron(II) hydroxide,	1.61%						
	Iron(III) nitrate nonahydrate	7.23%						
	3,6-Dimethyl-4-octyne-3,6-diol	0.30%						

(continued)

	Formulation		H^+ (%)	Fe^{2+} (%)	Fe^{3+} (%)	A/B	Etching rate (μm/minute)	Tensile shear strength (MPa)
Example 6	Sulfamic acid	1.94%	0.02	5.00	10.00	0.50	5.65	31.5
	Ammonium iron(II) sulfate hexahydrate	35.11%						
	Iron(III) chloride	29.05%						
	Potassium acetylenedicarboxylate	1.00%						
Example 7	Nitric acid (67.5%)	46.67%	0.50	3.00	2.00	1.50	2.33	35.4
	Iron(II) acetate	9.34%						
	Iron(III) hydroxide	3.18%						
	4-Diethylamino-2-butyn-1-ol	5.00%						
Example 8	Phosphoric acid (89%)	36.70%	1.00	0.20	1.00	0.20	1.61	28.7
	Iron(II) sulfate heptahydrate	1.00%						
	Iron(III) chloride	2.91%						
	5-Phenyl-4-pentyn-1-ol	0.01%						
Example 9	Sulfuric acid (62.5%)	31.36%	0.40	3.00	3.00	1.00	2.78	42.3
	Iron(II) sulfate heptahydrate	14,94%						
	Iron(III) sulfate pentahydrate	13.16%						
	1,4-Bis(2-hydroxyethoxy)-2-butyne	0.50%						

[Table 2]

	Formulation		H^+ (%)	Fe^{2+} (%)	Fe^{3+} (%)	A/B	Etching rate (μm/minute)	Tensile shear strength (MPa)
Comparative Example 1	Sulfuric acid (62.5%)	39.20%	0.50	0	3.00	-	2.66	18.1
	Iron(III) chloride	8.72%						
Comparative Example 2	Sulfuric acid (62.5%)	31.36%	0.40	0	3.00	-	3.04	19.7
	Iron(III) sulfate pentahydrate	13.16%						
	2,4-hexadiyne-1,6-diol	0.50%						

(continued)

	Formulation		H$^+$ (%)	Fe^{2+} (%)	Fe^{3+} (%)	A/B	Etching rate (μm/minute)	Tensile shear strength (MPa)
Comparative Example 3	Sulfuric acid (62.5%)	31.36%	0.40	3.00	0.00	-	0.18	16.2
	Iron(II) sulfate heptahydrate	14.94%						
	10,12-Pentacosadiynoic acid	0.50%						
Comparative Example 4	Sulfuric acid (98%)	65.00%	1.30	1.00	1.00	1.00	1.64	20.8
	Iron(II) hydroxide	1.61%						
	Iron(III) nitrate nonahydrate	7.23%						
Comparative Example 5	Phosphoric acid (89%)	29.36%	0.80	0.05	1.00	0.05	1.52	18.4
	Iron(II) sulfate heptahydrate	0.25%						
	Iron(III) hydroxide	1.59%						
	2,5-Dimethyl-3-hexyne-2,5-diol	0.10%						
Comparative Example 6	Phosphoric acid (89%)	29.36%	0.80	1.50	0.50	3.00	0.84	19.5
	Iron(II) sulfate heptahydrate	7.50%						
	Iron(III) hydroxide	0.80%						
	Potassium acetylenedicarboxylate	0.10%						
Comparative Example 7	Hydrochloric acid (35%)	1.00%	0.01	0	5.50	-	3.31	19.3
	40% Iron(III) chloride solution	40.00%						
	2-Propyn-1-ol	0.25%						
Comparative Example 8	No etching treatment (Acetone degreasing only)		-	-	-	-	-	12.7

[0049] FIGS. 2 to 4 are scanning electron microscope (SEM) observation photographs of the SPCC surfaces (acceleration voltage 20 kV, sample tilt angle 45°, magnification 3,500 times). FIG. 2 shows the SPCC surface of Example 9 after the treatment with the etching agent, FIG. 3 shows the SPCC surface of Comparative Example 8 after the treatment with the etching agent, and FIG. 4 shows the SPCC surface before the treatment (Comparative Example 8). It is apparent that the etched SPCC surfaces shown in FIGS. 2 and 3 have irregularities and thus have a surface area larger than that of the unetched SPCC surface shown in FIG. 4. A comparison between FIGS. 2 and 3 shows that the surface shown in FIG. 2, which was treated with the etching agent according to the invention, has sharp complicated irregularities between bumps shaped like mountain peaks, whereas the surface shown in FIG. 3 only has smooth irregularities between bumps shaped like mountain peaks and formed in a mesh-like pattern. It is conceivable that such characteristic irregularities uniformly formed on the surface of the steel material by the surface treatment with the etching agent of the invention have a high anchor effect (anchoring effect) to significantly improve the adhesion to the bonded material.

[0050] A careful study of the results in Tables 1 and 2 shows the following facts. The tensile shear strength of the joint part was about 20 MPa when the treatment was performed using the etching agent of each of Comparative Examples 1 to 4 and 7, which did not contain either the ferrous ions, the ferric ions, or the acetylene group-containing water-soluble compound (Table 2). The tensile shear strength was about 20 MPa also when the treatment was performed using the etching agent of Comparative Example 5 where the ratio A/B of the ferrous ion concentration (A) to the ferric ion concentration (B) is less than 0.1 or using the etching agent of Comparative Example 6 where the ratio A/B is more than 2.5. In contrast, the tensile shear strength was about 30 MPa or more in each of Examples 1 to 9 where the etching agent used contains ferrous ions, ferric ions, and an acetylene group-containing water-soluble compound and the ratio A/B is in the specified range. This shows that the resulting bonding strength is at least about 1.5 times higher in Examples 1 to 9 than in Comparative Examples 1 to 7.

Claims

1. An etching agent for steel, wherein
   the etching agent is an acidic aqueous solution containing: ferrous ion; ferric ion; and an acetylene group-containing water-soluble compound,
   a ferrous ion concentration of A% by weight and a ferric ion concentration of B% by weight satisfies a ratio A/B being from 0.1 to 2.5.

2. The etching agent according to claim 1, wherein the acetylene group-containing water-soluble compound is a chemical compound including an acetylene group and a hydroxy group.

3. The etching agent according to claim 1 or 2, wherein
   the ferric ion concentration is from 0.2 to 20% by weight, and
   a concentration of the acetylene group-containing water-soluble compound is from 0.01 to 5% by weight.

4. The etching agent according to any one of claims 1 to 3, wherein an acid concentration as a resulting hydrogen ion concentration in the etching agent is from 0.02 to 1.3% by weight.

5. The etching agent according to any one of claims 1 to 4, wherein the ferrous ion concentration is from 0.02 to 5% by weight.

6. A replenishing solution that is to be added to the etching agent according to any one of claims 1 to 5 for continuous or repeated use of the etching agent, wherein the replenishing solution includes an acetylene group-containing water-soluble compound.

7. The replenishing solution according to claim 6, wherein the replenishing solution is an acidic aqueous solution.

FIG. 1

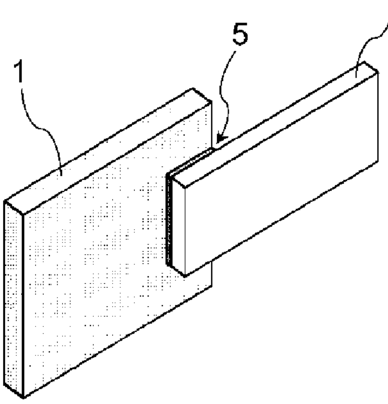


FIG. 2

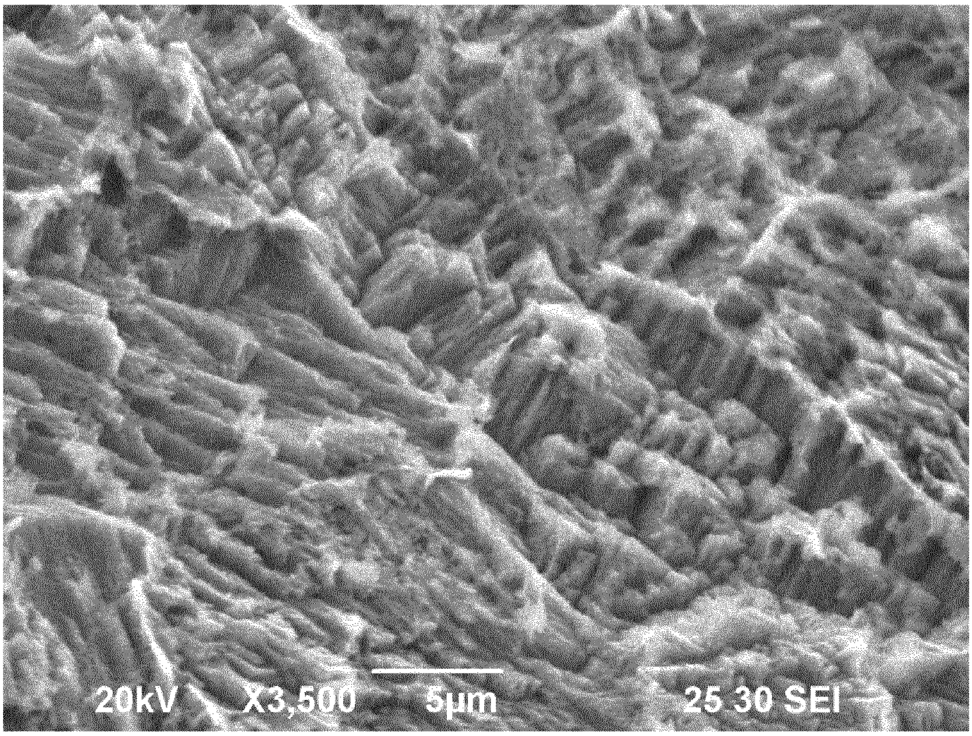


FIG. 3

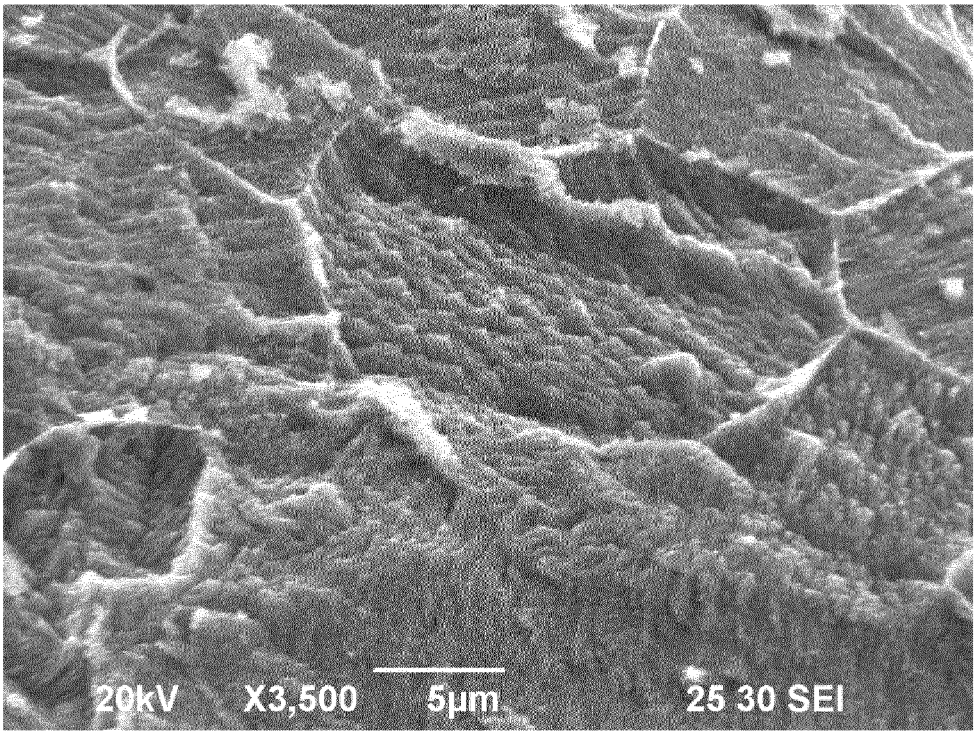
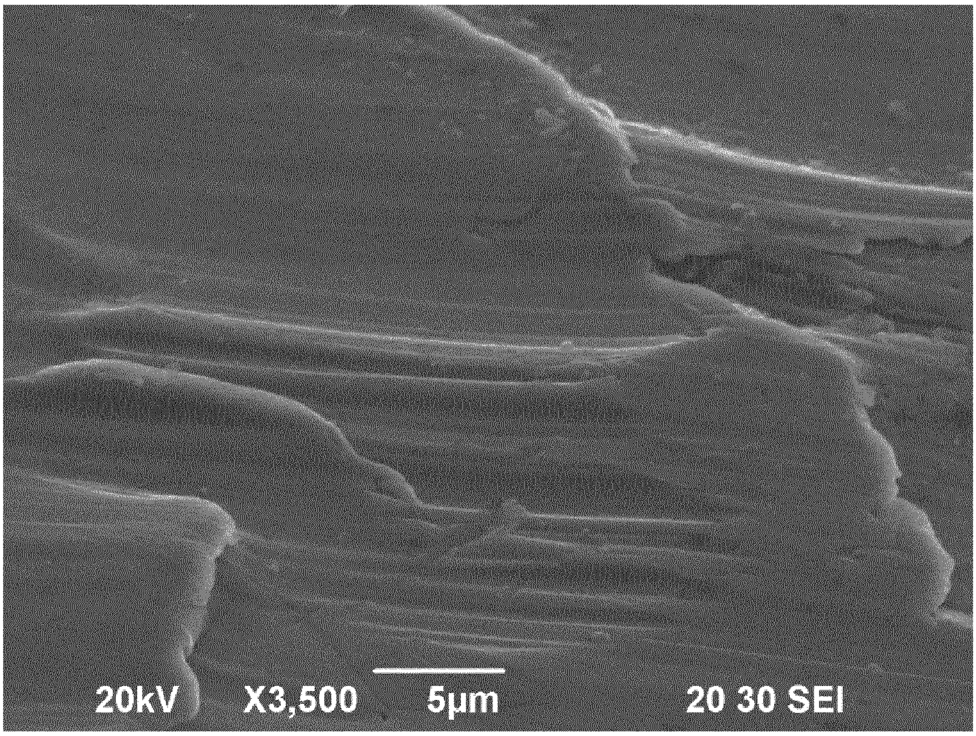


FIG. 4



INTERNATIONAL SEARCH REPORT	International application No. PCT/JP2015/066299

A. CLASSIFICATION OF SUBJECT MATTER
C23F1/28(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)
C23F1/28

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	1996-2015
Kokai Jitsuyo Shinan Koho	1971-2015	Toroku Jitsuyo Shinan Koho	1994-2015

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.
Y	JP 6-200385 A (Asahi Chemical Co., Ltd.), 19 July 1994 (19.07.1994), claims; paragraph [0002] (Family: none)	1-7
Y	JP 64-87788 A (Asahi Denka Co., Ltd.), 31 March 1989 (31.03.1989), claims; page 2, lower left column, lines 1 to 5; page 3, upper left column, lines 5 to 18 (Family: none)	1-7
X A	JP 1-301869 A (Dai-Ichi Kogyo Seiyaku Co., Ltd.), 06 December 1989 (06.12.1989), claims (Family: none)	6,7 1-5

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

*	Special categories of cited documents:
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"E"	earlier application or patent but published on or after the international filing date
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"&"	document member of the same patent family

Date of the actual completion of the international search 25 August 2015 (25.08.15)	Date of mailing of the international search report 08 September 2015 (08.09.15)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/066299

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	JP 2-141589 A (Dai-Ichi Kogyo Seiyaku Co., Ltd.), 30 May 1990 (30.05.1990), claims (Family: none)	6,7 1-5
A	JP 53-68643 A (Kozo YOSHIZAKI), 19 June 1978 (19.06.1978), entire text (Family: none)	1-7

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- WO 2008146833 A **[0003]**