

(12) **UK Patent Application** (19) **GB** (11) **2 179 058 A**  
(43) Application published 25 Feb 1987

(21) Application No **8616738**

(22) Date of filing **9 Jul 1986**

(30) Priority data

(31) **60/169219**

(32) **31 Jul 1985**

(33) **JP**

(51) INT CL<sup>4</sup>  
**C25D 5/10**

(52) Domestic classification (Edition I):

**C7B 120 304 719 721 724 727 737 739 BPK**

(56) Documents cited

**GB 1601057 US 3957452**

**Electroplating Engineering Handbook pages 185-187**

(71) Applicant

**Mitsubishi Cable Industries Ltd**

(Incorporated in Japan)

**8 Higashimukojima Nishino-cho, Amagasaki-shi, Hyogo-  
ken, Japan**

(72) Inventors

**Hideaki Shirai**

**Michio Hirose**

**Satoru Hayata**

**Yoshinori Takada**

**Hiroshi Ishibashi**

**Katsuo Nobu**

(74) Agent and/or Address for Service

**Matthews Haddan & Co,**

**Haddan House, 33 Elmfield Road, Bromley, Kent**

**BR1 1SU**

**(54) Aluminum composite material**

(57) Aluminum composite material which comprises an aluminum substrate, a primer coating comprising zinc and a heat stable metal e.g. Fe, Ni, Co, Cu, Cr and Mn, and an easily solderable metal deposit e.g. Cu, Ni, Sn and soft solder, which has voids generated by 400°C-void-detecting test of not more than 5 per 10 cm<sup>2</sup>. The aluminum composite material has an excellent heat resistance and contact electric resistance at a high temperature.

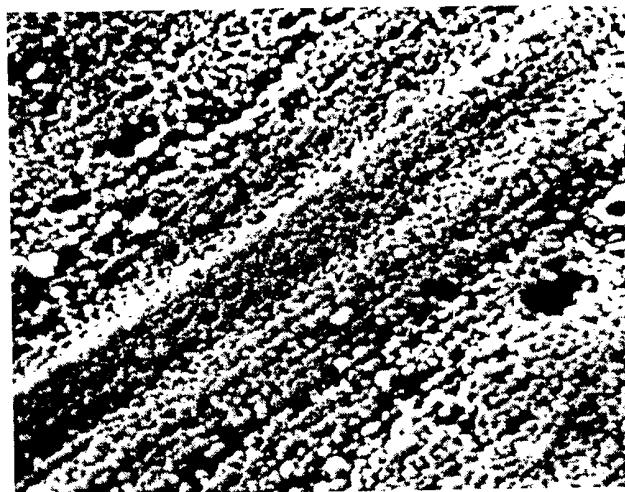
**GB 2 179 058 A**

2179058

Fig.1



Fig.2



## SPECIFICATION

## Aluminum composite material

5 The present invention relates to an aluminum composite material having a deposit of an easily solderable metal such as copper and, more particularly, to an aluminum composite material comprising an aluminum substrate, a primer coating formed on the aluminum substrate and a deposit of an easily solderable metal formed on the primer coating. 5

An aluminum material has a disadvantage that the aluminum is hardly soldered. However, an 10 aluminum composite material having a deposit of an easily solderable metal such as copper is industrially useful as various structural materials or various parts of electric and electronic devices, since the aluminum composite material can maintain advantages of aluminum, i.e. good heat conductivity, good electrical conductivity, lightness in weight, low price and the like, as they are. 10

However, if an aluminum substrate is directly plated with, for example, copper, a copper 15 deposit having a good adhesion cannot be obtained. Accordingly, heretofore, prior to the plating of the aluminum substrate with copper, a zinc coating is deposited on the aluminum substrate by means of zincate treatment, and then the copper deposit is plated on the zinc coating. There is a problem, however, that the copper deposit obtained by the treatment with the conventional zincate-treating composition containing a zinc compound as a principal component is peeled off 20 in ease at a high temperature. Recently, various zincate-treating compositions including compounds of a metallic element having heat resistance such as iron or nickel, and various zincate-treating methods have been developed. As a result, formation of the copper deposit having an excellent peeling-off resistance at a high temperature so as to satisfy the heat resistance test according to JIS H 8504-1984, 13.1 can be realized. 20

25 At present, electric devices and electronic devices tend to be miniaturized and various electric circuits tend to be highly integrated, and as a result requirements on the heat resistance of the copper deposit becomes further severe. Due to such severe requirements, the heat resistance of the conventional aluminum composite material with the copper deposit, so called high grade heat resistive articles on market is insufficient. 25

30 For instance, when the above described composite material is used for control circuits of robot used at a high temperature, the control circuits are exposed to a high temperature of not less than 100°C for a long period of time from several weeks to several months under a normal pressure or a high pressure. In this case, there is a problem that electric resistance at the interface between the copper deposit and the aluminum substrate increases with lapse of time, 35 since the adhesion of the copper deposit is gradually reduced due to the heating for a long period of time. There is possibility that the increase of the interfacial electric resistance causes mismovement of the robot when the composite material is used at control circuits and the like. 35

Further, in another use, the aluminum composite material with copper deposit is used under conditions that the composite material is repeatedly and rapidly heated and cooled between a 40 very low temperature of about -50°C and a high temperature of not less than 100°C. In this case, such repeated thermal shock also causes the copper deposit of the conventional high grade heat resistive articles to be peeled off. 40

In addition, in many cases, the composite material is soldered with parts of other electronic devices on the copper deposit. In these cases, the adhesion of the copper deposit is reduced 45 due to the local heating during the soldering. Therefore, the copper deposit also tends to be peeled off. 45

When the copper deposit is formed on the aluminum substrate, the formation is generally carried out according to the following procedures. The surface of the aluminum substrate is firstly pretreated in order to remove fats and aluminum oxides, so that the surface is cleaned. A 50 zinc coating is then deposited by means of zincate-treatment. Finally, copper is deposited on the zinc primer coating by means of electroplating method or electroless plating method. 50

From the present inventors' investigations, when the above pretreatment is insufficient, a very small amount of gas, water and the like, remains on the surface of the aluminum substrate and at the interface between the aluminum substrate and the zinc coating and the like, and those 55 residues expand at a high temperature, whereby the adhesion of the copper deposit to the aluminum substrate is gradually reduced. Further, even in case of the commercially available heat stable articles which are conventionally estimated as voidless articles, when those articles are evaluated according to the 400°C-void-detecting method defined hereinafter, which is newly established by the present inventors, the number of generated voids widely varies. In that case, 60 the articles having a void value of more than a certain value clearly shows a low heat resistance. 60

In addition, various zincate-treating compositions and zincate-treating methods have been proposed and put to practical use. However, when failing to select the zincate treating composition and the zincate-treating method, pinholes are formed in the zinc primer coating formed by the treatment. Further, the surface of the zinc primer coating becomes rough and largely concave 65 and convex since zinc is deposited in the form of gross particles. 65

These pinholes tend to cause voids to remain. However, the large roughness and unevenness of the surface is disadvantage in adhesion between the zinc primer coating and the copper deposit because a surface having a large roughness and unevenness has a smaller surface area than a surface having a fine and small unevenness, and thus the adhesion area of the zinc primer coating to the copper deposit is smaller. Accordingly, the adhesive force therebetween is gradually reduced and the copper deposit is occasionally peeled off due to an inner force generated from the expandable residue and the temperature rising. 5

The object of the present invention is to provide an aluminum composite material having a deposit of an easily solderable metal, which has a high peeling off resistance against continuous use at a high temperature, a thermal shock and the like, in order to satisfy the above-mentioned recent severe requirements. 10

In accordance with the present invention, there is provided an improved aluminum composite material comprising an aluminum substrate, a primer coating formed on the aluminum substrate and an easily solderable metal deposit formed on the primer coating, the improvement is that the primer coating comprises zinc and a heat stable metal, and that the number of voids observed on the easily solderable metal deposit is not more than 5 per 10 cm<sup>2</sup> in 400°C-void-detecting test. 15

In the aluminum composite material of the present invention, the primer coating must include the heat stable metal other than zinc. The heat stable metal contributes to the refinement of zinc precipitated from a zincate-treating composition. As a result, a zinc primer coating having a surface with many fine concave and convex portions and without pinholes can be formed. Thus, from the above-mentioned reason, the adhesion force between the surface of the primer coating and the easily solderable metal deposit formed thereon can be increased. 20

Further, in the present invention, the aluminum composite material must have the number of voids observed on the solderable metal deposit of not more than 5 per 10 cm<sup>2</sup> in the 400°C-void-detecting test. According to the 400°C-void-detecting test a very small amount of the expandable residual substances which have been heretofore overlooked can be detected. When the number of voids detected according to the test is not more than 5 per 10 cm<sup>2</sup>, preferably not more than 2 per 10 cm<sup>2</sup>, most preferably not more than 1 per 10 cm<sup>2</sup>, the zinc primer coating containing the heat stable metal shows an excellent heat resistance. 25

The 400°C-void-detecting test is a test that the present inventors has newly established in order to estimate a high temperature adhesion of an aluminum composite material. The test is carried out according to the following procedures and conditions. 30

[400°C-void-detecting test]

35 A sample of 10 cm square is put in an oven of 400°C and is maintained at that temperature for 10 minutes and, thereafter, the sample is rapidly cooled by dipping into water of normal temperature in order to generate expansion in or under the easily solderable metal deposit. Among the expanded projections observed on the surface of the solderable metal deposit, one which has a major axis of not less than 0.2 mm is defined as "void", and the number of voids is counted. 40

Figures 1 and 2 are microscopic photographs (x3,000) by using a scanning electron microscope showing surfaces of the primer coatings formed in Example 10 and Comparative Example 3, respectively.

In the present invention, it is preferable that the primer coating is as dense as possible, and that the surface of the primer coating has granular projections as many as possible and as fine as possible. Particularly, it is preferable that when observing the granular projections which are deposited during the zincate-treatment, with a scanning electron microscope (magnification 3,000), the number of projections is at least  $1 \times 10^6$  per mm<sup>2</sup>, particularly at least  $3 \times 10^6$  per mm<sup>2</sup>. Further, at the above magnification, there is a case where the superfine granular projections are uniformly distributed so that the surface is observed like a smooth surface. Such a state of surface is particularly preferable. 45

The primer coating comprises zinc and a heat stable metal. The heat stable metal can provide a primer coating having a dense structure without pinholes and contributes to the realization of the above-mentioned surface.

55 Metals having a melting point of not less than around 800°C, preferably not less than 1,000°C, particularly not less than 1,200°C can be used as the heat stable metal. Examples of the heat stable metal are for instance, at least one member selected from the group consisting of Fe, Ni, Co, Cu, Cr and Mn. Preferable combination of metals is a Zn-Fe-Ni system, a Zn-Fe-Co system, a Zn-Fe-Ni-Co system, or the like. However, other combinations can be optionally employed according to the required heat resistance, or the like. 50

The total content of the heat stable metal is 0.1 to 50 % (% by weight, hereinafter the same), preferably 3 to 30 %. When the total content is less than 0.1 %, it is hard to make the primer coating dense. When the total content is more than 50 %, the affinity between the primer coating and the aluminum substrate is reduced, so that good adhesion cannot be obtained.

60 The amounts (% by weight) of zinc and the heat stable metal of the primer coating can be 65

measured, for example, by X-ray microanalyzer (EPMA).

The amounts of zinc and each heat stable metal vary depending on desired use, required heat resistance, quality of the aluminium substrate and the like, and can be optionally selected by experiments corresponding to each requirement.

5 Preferable amount of each heat stable metal is as follows: Fe being 0.5 to 30 %, preferably 1 to 15 %; Ni being 0.5 to 40 %, preferably 1 to 30 %; Co being 0.5 to 30 %, preferably 1 to 20 %; Cu being 0.05 to 20 %, preferably 0.1 to 15 %; Cr being 0.05 to 20 %, preferably 0.1 to 15 %; and Mn being 0.01 to 20 %, preferably 0.1 to 15 %.

Various soft or hard aluminum materials such as a pure aluminum, a secondary aluminum or an 10 aluminum alloy can be used as the aluminum substrate. Preferable examples of the aluminum 10 alloy, for instance, are 2014, 3003, 5052, 6063, 6101 and the like. Also, a high strength aluminum can be used. The high strength aluminum has a tensile strength of around 20 kg/mm<sup>2</sup> or more, a bearing force of around 15 kg/mm<sup>2</sup> or more, and an elongation of around 20 % or less. When the high strength aluminum is used, the obtained aluminum composite material is 15 improved in bending resistance.

The shape of the aluminum substrate is not particularly limited insofar as the primer coating 15 and the easily solderable metal deposit can be formed on the aluminum substrate. Examples of the shape are, for instance, plate, wire, rod, foil, hoop or block. Further, an aluminum substrate proceeded in various shapes such as box by means of punching, cutting, die casting or the like, 20 can also be used. Accordingly, the thickness of the aluminum substrate is not particularly limited.

Examples of the metal of the solderable metal deposit formed on the primer coating are, for 20 instance, noble metals such as Cu, Ag, Au and a metal of Pt group; soft solders such as common solder, tinsmith solder and plumber's solder; and other easily solderable metals such as Ni, Sn and Pb.

25 The thickness of the primer coating and the thickness of the solderable metal deposit can be optionally selected depending on use. In general, the thickness of the primer coating is 0.005 to 2  $\mu$ m, preferably 0.01 to 0.1  $\mu$ m. The thickness of the metal deposit is 1 to 40  $\mu$ m, preferably 3 to 20  $\mu$ m.

Further, if desired, on the metal deposit another metal deposit of an easily solderable metal 30 different from the metal of the above-mentioned metal deposit may be formed. The thickness of the primer coating can be measured, for example, by electrolytic method mentioned hereinafter.

A process for preparing the aluminum composite material of the present invention is described hereinbelow.

Though the preferable process of the present invention is described later, the aluminum 35 composite material of the present invention can be prepared by basically employing known methods for pretreatment of a surface of an aluminum substrate, known zincate-treating compositions containing heat stable metal salts, known methods for zincate-treatment and known plating methods of an easily solderable metal, as they are. However, the point essentially different from the preparation procedures in the conventional high grade heat stable articles and 40 to be payed attention is to perform each step, particularly the pretreating step, carefully and faithfully to the fundamental procedures.

In this connection, the conventional aluminum composite materials do not have enough heat 45 resistance which is the object of the present invention in spite of the fact that the conventional composite materials are prepared by employing the above-mentioned known pretreating method, zincate-treating method and metal plating method. The major reason is seemed in that the conventional recognition relating to the estimation standard of heat resistance is considerably insufficient. From economical point of view, the manufactures always take up position that process steps should be simplified as much as possible within the estimation standard. Accordingly, for example, surfaces of aluminum substrates to be zincate-treated is usually cleaned to 50 the minimum extent and, therefore, a very small amount of fats, aluminum oxides and the like is remained on the surfaces even after cleaning. These residues cause the generation of the voids.

Various aluminum substrates can be used in the preparation of the aluminum composite 55 material of the present invention, as described above. However, it is desirable that the use of aluminum substrates having a number of flaws or stains on their surfaces and having an uneven oxide film or the like is avoided, or that those substrates should be used after polishing.

The aluminum substrate is cleaned with a caustic alkali such as an aqueous solution of sodium hydroxide or an aqueous solution of potassium hydroxide. By the cleaning procedure, dusts and fats depositing on the surface of the aluminum substrate at the same time when the aluminum oxide film thereon is dissolved. It is preferable that the aluminum substrate is treated with an 60 aqueous solution of caustic alkali having a certain high concentration, e.g. 10 to 170 g/l at normal temperature to 90°C in order to remove the aluminum oxide film more surely. Further, when a small amount of a surfactant such as a nonion surfactant is added to the aqueous solution of caustic alkali, even insides of fine recesses on the surface can be cleaned. After the cleaning, the cleaning solution of caustic alkali depositing on the surface of the aluminum 65 substrate is washed with an aqueous solution of nitric acid and, thereafter, the aqueous solution

of nitric acid is removed by washing with water.

The cleaned aluminum substrate is then zincate-treated.

The zincate-treating composition fundamentally comprises water-soluble zinc compound, a water-soluble compound of a heat stable metal, a caustic alkali and water.

5 The water-soluble zinc compound and the water-soluble compound of the heat stable metal are sources for supplying the metal components of the primer coating. Examples of the water-soluble zinc compound are, for instance, zinc sulfate, zinc oxide, zinc nitrate, zinc carbonate, zinc chloride, and the like. 5

As the water-soluble compound of the heat stable metal, various compounds can be used.

10 Examples of the compound for supplying Fe are, for instance, ferrous chloride, ferric chloride, iron sulfate, iron nitrate, ferrous oxide, ferric oxide, and the like. Examples of the compound for supplying Ni are, for instance, nickel sulfate, nickel hydroxide, nickel oxide, nickel nitrate, nickel chloride, and the like. Examples of the compound for supplying Cr are, for instance, chromium sulfate, chromium oxide, chromium nitrate, chromium chloride, and the like. 10

15 Examples of the compound for supplying Co are, for instance, cobalt sulfate, cobalt oxide, cobalt nitrate, cobalt hydroxide, cobalt chloride, and the like. Examples of the compound for supplying Cu are, for instance, copper sulfate, copper oxide, copper chloride, copper carbonate, copper cyanide, copper hydroxide, copper nitrate, and the like. Examples of the compound for supplying Mn are, for example, manganese oxide, manganese sulfate, manganese carbonate, manganese 15

20 chloride, manganese hydroxide, manganese nitrate, and the like. 20

The ratio of amounts of the water-soluble zinc compound and the water soluble compound of the heat stable metal, and also the ratio of amounts of the water-soluble compounds of the heat stable metals are decided depending on the desired composition of the primer coating. In general, it is preferable that the amount of the water-soluble zinc compound is 2 to 200 g/l and

25 the total amount of the water-soluble compounds of the heat stable metal is 0.05 to 100 g/l. 25

Other than the above-mentioned components, a caustic alkali is generally added thereto. The caustic alkali such as NaOH and KOH is a component for dissolving a thin layer of an oxide film formed on the surface of the aluminum substrate after the above-mentioned surface cleaning treatment in order to assist the formation of a stable primer coating on the aluminum substrate.

30 In general, the concentration is preferably 30 to 500 g/l. 30

In order to promote denseness of the primer coating, it is preferable that an agent for forming complex compound, an agent for promoting denseness such as an alkali metal cyanide salt are further added.

35 The agent for forming complex compound is a component so that the metal components form complex ions to prevent the heat stable metal from precipitating and so that a dense primer coating is formed on the surface of the aluminum substrate by a synergic effect of the complex ions and the other components. 35

Examples of the agent for promoting denseness are, for instance, oxycarboxylic acids such as tartaric acid, lactic acid and citric acid, and alkali metal salts thereof; polycarboxylic acids such

40 as nitrilotriacetic acid, iminodiacetic acid and EDTA, and alkali metal salts thereof; amines such as monoethanolamine, ethylenediamine and triethanolamine; alkali metal cyanides such as KCN and NaCN; metal salts such as alkali metal salts of carbohydrates. Examples of the carbohydrate are, for instance, monosaccharides such as D-erythro-2-ketopentose, D-threo-2-ketopentose, L-erythro-2-ketopentose, D-fructose, D-tagatose, L-fructose, D-psicose, L-psicose, D-erythrose, D- 40

45 threose, L-glucose and D-galactose; oxide products of monosaccharides such as D-gluconic acid and saccharic acid; reduction products of monosaccharides such as sorbitol; and the like. In general, the concentration of the agent for promoting denseness is preferably 1 to 150 g/l. 45

The primer coating is formed by dipping the aluminum substrate into the above-mentioned zincate-treating composition. In case of using the agent for promoting denseness, the tempera-

50 ture of the zincate-treating composition is 0° to 60°C, preferably 10° to 40°C, and the time for dipping is 10 seconds to 5 minutes, preferably 30 seconds to 1 minute. In case of not using the agent for promoting denseness such as the agent for forming complex compound, the temperature of the zincate-treating composition is a relatively low temperature, e.g. in general 5° to 30°C, preferably 10° to 20°C. 50

55 The primer coating may be formed by a vacuum evaporation method, a spattering method, an electroplating method or the like, other than the abovementioned method. 55

The aluminum composite material of the present invention is obtained by forming a deposit of an easily solderable metal on the primer coating. In the plating method of the easily solderable metal, plating conditions employed in the conventional plating of each easily solderable metal can

60 be employed. 60

The present invention is more specifically described and explained by means of the following Examples. It is to be understand that the present invention is not limited to the Examples and various changes and modifications may be made in the invention without departing from the spirit and scope thereof.

*Examples 1 to 16 and Comparative Examples 1 to 8*

Pretreatment of an aluminum substrate was carried out in the following procedures. An aluminum substrate having a length of 50 cm, a width of 20 cm and a thickness of 1.5 mm was treated in an alkali bath (NaOH: 16 g/l, Na<sub>2</sub>CO<sub>3</sub>: 27 g/l) under the conditions shown in

5 Table 1 and, thereafter, washed with rushing water under the conditions shown in the same Table. Then, the aluminum substrate was acid-pickled with a 40 % aqueous solution of nitric acid under the conditions shown in Table 1 and thereafter, washed with rushing water under the conditions shown in the same Table.

A primer coating was formed on the pretreated surface of the aluminum substrate by dipping 10 the aluminum substrate in a zincate-treating composition (30°C) having a formulation shown in Table 2 for 1 minute. The metal content, the thickness and the number of granular projections of the formed primer coating are shown in Table 3.

The metal contents of the primer coating were measured by using X-ray microanalyzer (available from NIHON DENSHI CO., LTD. as JXA-50A) under the following conditions, and determined by comparing with a standard sample.

Acceleration voltage: 25 KV

Absorption current: 10<sup>-8</sup>A

Spectrocrystal: LiF

Counter: GFPC (gass flow proportional counter)

20 Applied voltage of GFPC: 1.6 KV

The number of granular projections per 1 mm<sup>2</sup> was counted by using a scanning electron microscope (available from NIHON DENSHI CO., LTD. as JXA-50A) at a magnification of 3,000.

The primer coating in the present invention has a dense and flat surface. For example, the state of the surface of the primer coating formed in Example 10 is shown in Fig. 1 which is a 25 microscopic photograph (X3,000) with the scanning electron microscope. As shown in Fig. 1, each metal component of the primer coating forms an alloy-like dense structure.

On the other hand, as shown in Fig. 2 (a microscopic photograph (X3,000) of the surface of the primer coating formed in Comparative Example 3 with the scanning electron microscope), the surface is in the state that a number of successive particles are deposited. Therefore, it is

30 impossible to avoid the generation of many voids at a high temperature.

Then, the aluminum substrate with the primer coating was electroplated with copper, nickel, common solder or tin under the following conditions to form a metal deposit having a thickness shown in Table 3.

(Copper plating)

35 Plating bath: CuCn (60 g/l) and NaCN (60 g/l)

Temperature : 80°C

Current density: 3A/dm<sup>2</sup>

Applied time of current: 8 minutes

(Common solder plating)

40 Plating bath: 47 % aqueous solution of Sn(BH<sub>4</sub>)<sub>2</sub>

(200 g/l), 50 % aqueous solution of Pb(BH<sub>4</sub>)<sub>2</sub> (50 g/l) and 42 % aqueous solution of HBH<sub>4</sub> (100 g/l)

Temperature: 25°C

45 Current density: 2A/dm<sup>2</sup>

Applied time of current; 10 minutes

(Nickel plating)

Plating bath: NiSO<sub>4</sub> (240 g/l), NiCl<sub>2</sub> (45 g/l) and H<sub>2</sub>BO<sub>3</sub> (30 g/l)

50 Temperature: 50°C

Current density 3A/dm<sup>2</sup>

Applied time of current: 10 minutes

(Tin plating)

Plating bath: Na<sub>2</sub>SnO<sub>3</sub> (150 g/l) and NaOH (20 g/l)

55 Temperature: 60°C

Current density: 2A/dm<sup>2</sup>

Applied time of current: 21 minutes

Then, with respect to each aluminum composite material, the following two void-detecting tests were carried out. The results are shown in Table 3.

60 (1) Void-detecting test according to JIS H 8504-1984, 13.1

This test was carried out at 250°C.

(2) 400°C-void detecting test established by the present inventors

The procedures and conditions are aforementioned.

Table 1  
Condition of Pretreatment

Alkali Cleaning			Pickling		
Temperature ( $^{\circ}$ C)	Time (sec.)	Time for Water-Washing (sec.)	Temperature ( $^{\circ}$ C)	Time (sec.)	Time for Water-Washing (sec.)
Ex. 1	45	60	60	60	60
Ex. 2	45	60	60	"	60
Ex. 3	45	60	60	"	60
Ex. 4	45	60	60	"	60
Ex. 5	45	60	60	"	60
Ex. 6	45	60	60	"	60
Ex. 7	45	60	60	"	60
Ex. 8	45	60	60	"	60
Ex. 9	45	60	60	"	60
Ex. 10	45	60	60	"	60
Ex. 11	45	60	60	"	60
Ex. 12	45	60	60	"	60
Ex. 13	45	60	60	"	60
Ex. 14	45	60	60	"	60
Ex. 15	45	60	60	"	60
Ex. 16	45	60	60	"	60

- continued -

- continued -

Condition of Pretreatment

Alkali Cleaning			Pickling		
Temperature (°C)	Time (sec.)	Time for Water-Washing (sec.)	Temperature (°C)	Time (sec.)	Time for Water-Washing (sec.)
Com. Ex. 1	45	60	60	Normal temperature	60
Com. Ex. 2	normal temperature	15	20	"	30
Com. Ex. 3	"	15	20	"	30
Com. Ex. 4	"	15	20	"	30
Com. Ex. 5	"	10	20	"	30
Com. Ex. 6	"	10	20	"	30
Com. Ex. 7	"	10	20	"	30
Com. Ex. 8	"	10	20	"	30

Table 2  
Zincate-treating Composition (g/l)

Zincate-treating composition No.	ZnO	ZnSO <sub>4</sub> · 7H <sub>2</sub> O	FeCr <sub>3</sub>	NiSO <sub>4</sub> · 6H <sub>2</sub> O	CuSO <sub>4</sub> · 7H <sub>2</sub> O	Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> · 3H <sub>2</sub> O	MnSO <sub>4</sub> · 4 to 5H <sub>2</sub> O
1	-	40	3	20	-	-	-
2	-	60	2	5	-	-	-
3	-	60	3	-	5	-	-
4	-	60	2	-	10	-	-
5	-	60	-	20	3	-	-
6	-	60	-	10	-	5	-
7	-	60	3	-	-	10	-
8	-	60	3	10	-	-	5
9	-	40	1	2	2	-	-
10	-	60	2	5	3	-	-
11	-	80	3	20	5	-	-
12	20	-	2	5	1	-	-
13	50	-	-	-	-	-	-
14	20	-	-	-	-	20	-
15	-	60	-	1	-	-	-
16	-	60	1	2	2	-	-

- continued -

- continued -

Zincate- treating composi- tion No.	Zincate-treating Composition (g/l)			Ex. and Com. Ex.
	KCN	Potassium tartrate	Sodium gluconate	
1	-	20	5	120 Ex. 1 and Com. Ex. 5 and 6
2	-	30	10	140 Ex. 2
3	-	30	5	140 Ex. 3
4	-	30	10	180 Ex. 4
5	-	20	10	120 Ex. 5
6	10	30	20	140 Ex. 6 and Com. Ex. 7
7	-	30	30	180 Ex. 7
8	-	30	20	140 Ex. 8, 15 and 16
9	-	40	10	100 Ex. 9
10	-	40	5	140 Ex. 10, 13 and 14
11	-	40	5	180 Ex. 11
12	-	30	5	200 Ex. 12 and Com. Ex. 8
13	-	-	-	400 Com. Ex. 1
14	20	10	-	140 Com. Ex. 2
15	-	20	-	160 Com. Ex. 3
16	-	-	-	140 Com. Ex. 4

Table 3  
Construction of Aluminum Composite Material

	Primer Coating						Thickness ( $\mu\text{m}$ )	The number of granular projections (per $\text{mm}^2$ )
	Zn	Fe	Ni	Co	Cu	Cr		
Ex. 1	59	7	38	-	-	-	0.03	$5 \times 10^6$
Ex. 2	87	4	9	-	-	-	0.03	$4 \times 10^6$
Ex. 3	87	7	-	7	-	-	0.03	$7 \times 10^6$
Ex. 4	83	4	-	13	-	-	0.03	$6 \times 10^6$
Ex. 5	61	-	35	4	-	-	0.03	$4 \times 10^6$
Ex. 6	79	-	13	-	8	-	0.03	$3 \times 10^6$
Ex. 7	80	6	-	-	-	14	-	0.03
Ex. 8	75	6	12	-	-	-	7	0.03
Ex. 9	89	3	4	4	-	-	-	$7 \times 10^6$
Ex. 10	85	4	7	4	-	-	-	$11 \times 10^6$
Ex. 11	73	4	18	4	-	-	-	$12 \times 10^6$
Ex. 12	89	-	4	6	1	-	-	$14 \times 10^6$
Ex. 13	85	4	7	4	-	-	0.03	$14 \times 10^6$
Ex. 14	85	4	7	4	-	-	0.03	$14 \times 10^6$
Ex. 15	75	6	12	-	-	-	7	$7 \times 10^6$
Ex. 16	75	6	12	-	-	-	7	$7 \times 10^6$

- continued -

- continued -

## Construction of Aluminum Composite Material

	Content (% by weight)					Thickness ( $\mu\text{m}$ )	The number of granular projections (per $\text{mm}^2$ )
	Zn	Fe	Ni	Co	Cu		
Primer Coating							
Com. Ex. 1	100	-	-	-	-	-	0.4
Com. Ex. 2	47	-	-	-	53	-	0.15
Com. Ex. 3	98	-	2	-	-	-	0.16
Com. Ex. 4	92	2	3	3	-	-	0.08
Com. Ex. 5	59	7	38	-	-	-	0.03
Com. Ex. 6	59	7	38	-	-	-	0.03
Com. Ex. 7	79	-	13	-	8	-	0.03
Com. Ex. 8	89	-	4	6	1	-	0.03
							$5 \times 10^5$
							$1 \times 10^6$
							$2 \times 10^6$
							$8 \times 10^5$
							$7 \times 10^6$
							$8 \times 10^6$
							$3 \times 10^6$
							$4 \times 10^6$

- continued -

- continued -

Construction of Aluminum Composite Material			
Easily solderable metal deposit		The number of voids (/10 cm <sup>2</sup> )	
Kind of metal	Thickness ( $\mu\text{m}$ )	JIS method (250°C)	400°C-Void-detecting method
Ex. 1	Cu	10	0
Ex. 2	Cu	10	0
Ex. 3	Cu	10	0
Ex. 4	Cu	10	0
Ex. 5	Cu	10	0
Ex. 6	Cu	10	0
Ex. 7	Cu	10	0
Ex. 8	Cu	10	0
Ex. 9	Cu	10	0
Ex. 10	Cu	10	0
Ex. 11	Cu	10	0
Ex. 12	Cu	10	0
Ex. 13	Ni	6	0
Ex. 14	common solder	10	0
Ex. 15	Ni	6	0
Ex. 16	Sn	10	0

- continued -

- continued -

Construction of Aluminum Composite Material

Easily solderable metal deposit		The number of voids (/10 cm <sup>2</sup> )	
Kind of metal	Thickness ( $\mu\text{m}$ )	JIS method (250°C)	400°C-Void-detecting method
Com. Ex. 1	Cu	10.3	12
Com. Ex. 2	Cu	10.2	7
Com. Ex. 3	Cu	10.9	1
Com. Ex. 4	Cu	10.8	2
Com. Ex. 5	Cu	10.6	0
Com. Ex. 6	Cu	10.2	0
Com. Ex. 7	Cu	10.1	0
Com. Ex. 8	Cu	10.5	0

With respect to the aluminum composite materials prepared in Examples 1 to 16 and Comparative Examples 1 to 8, the following tests were carried out. The results are shown in Table 4. (P.C.T. test)

5 Each test piece was heated in steam of 121°C under 2 atm for 2,000 hours and dried. Then, a contact electric resistance ( $\Omega$ ) was measured by means of a four-terminal network method at normal temperature. The change (%) of the contact resistance from the initial value of each test piece was measured. 5

10 (High temperature retaining test) Each test piece was heated in hot air of 150°C for 1,000 hours. Similar to P.C.T. test, each test piece was estimated by measuring the change (%) of the contact resistance from the initial value. 10

15 (Thermal shock test) This test was carried out according to the thermal shock test defined in EIAJ, SD-121-1979. The lower temperature side was an alcholol bath of -40°C and the higher temperature side was hot water bath of 100°C. A cycle of heating and cooling was repeated 1,000 times. The time for transferring between both bathes was not more than 5 seconds. Similar to P.C.T. test, each test piece was estimated by measuring the change (%) of the contact resistance from the initial value. 15

20 (Soldering test) Each test piece was soldered 50 times according to the soldering test defined in JIS H 8504-1984, 15.2. Each test piece was estimated by measuring the ratio (%) of the peeled metal deposit. 20

Table 4

	P.C.T. test [change of contact resistance (%)]	High temperature retaining test [change of contact resistance (%)]	Thermal shock test [change of contact resistance (%)]	Soldering test [Ratio (%)]
Ex. 1	0.0	0.0	0.1	0
Ex. 2	0.0	0.0	0.1	0
Ex. 3	0.2	0.2	0.3	0
Ex. 4	0.1	0.2	0.3	0
Ex. 5	0.2	0.3	0.2	0
Ex. 6	0.7	0.9	0.0	0
Ex. 7	0.7	0.8	0.1	0
Ex. 8	0.8	0.7	0.9	0
Ex. 9	0.0	0.1	0.4	0
Ex. 10	0.0	0.0	0.1	0
Ex. 11	0.0	0.0	0.1	0
Ex. 12	0.2	0.3	0.8	0
Ex. 13	0.3	0.2	0.6	0
Ex. 14	0.1	0.3	0.7	0
Ex. 15	0.2	0.2	0.8	0
Ex. 16	0.1	0.3	0.7	0

- continued -

- continued -

P.C.T. test [change of contact resistance (%)]		High temperature retaining test [change of contact resistance (%)]	Thermal shock test [change of contact resistance (%)]	Soldering test [Ratio (%)]
Com. Ex.	18	23	30	12
Com. Ex.	13.5	14.1	18.4	8
Com. Ex.	14.8	15.9	19.2	8
Com. Ex.	13.2	13.2	14.3	4
Com. Ex.	11.9	13.1	15.8	6
Com. Ex.	10.8	11.4	13.4	4
Com. Ex.	11.3	10.9	13.2	4
Com. Ex.	10.5	11.0	13.8	4

According to the present invention, there can be provided an aluminum composite material having an excellent peeling resistance and a stable contact resistance even if the composite material is exposed to a high temperature circumstance for a long time and even if a thermal shock is applied. The composite material can be easily soldered. Further, aluminum composite 5 materials having various shapes can be prepared, since the present invention can be applied to aluminum substrates having various shapes. 5

#### CLAIMS

1. An aluminum composite material comprising an aluminum substrate, a primer coating 10 formed on said aluminum substrate and a deposit of an easily solderable metal formed on said primer coating, said primer coating comprising zinc and a heat stable metal, and the number of voids observed on said deposit is not more than 5 per  $10\text{ cm}^2$  in  $400^\circ\text{C}$ -void-detecting test. 10
2. The composite material of Claim 1, wherein the thickness of said primer coating is 0.005 to  $2\text{ }\mu\text{m}$ .
3. The composite material of Claim 1, wherein said primer coating has granular projections of 15 at least  $1 \times 10^6$  per  $\text{mm}^2$  on its surface to be plated, when observing with a scanning electron microscope at a magnification of 3,000.
4. The composite material of Claim 1, wherein an element of said heat stable metal is at least one member selected from the group consisting of Fe, Ni, Co, Cu, Cr and Mn.
5. The composite material of Claim 4, wherein the total content of the element or the 20 elements of said heat stable metal is 0.1 to 50 % by weight.
6. The composite material of Claim 1, wherein said easily solderable metal is a member selected from the group consisting of Cu, Ni, Sn and Soft solder.
7. The composite material of Claim 1, wherein said primer coating consists of Zn-Fe-Co.
8. The composite material of Claim 1, wherein said primer coating consists of Zn-Fe-Ni. 25
9. The composite material of Claim 1, wherein said primer coating consists of Zn-Fe-Ni-Co.
10. An aluminum composite material as claimed in Claim 1, substantially as described herein with reference to any one of the examples.