

A STRIP COMPOSITE MATERIAL AND
A METHOD AND APPARATUS FOR ITS MANUFACTURE

5 The invention relates to a strip composite material
according to the preamble of Claim 1

10 A specific adjustment of the thickness of the
intermetallic phase (IMP) occurs in hot-tinned strips
through a subsequent heat treatment in hood-type,
through-type, or suspended-conveyor furnaces at
15 temperatures between 150°C to 180°C and annealing times,
for example, in hood-type furnaces of about 16 h. In
galvanically tinned strips there takes place an
additional reflow treatment with IR-radiation or hot air
in order to achieve through a remelting of the tin a
20 better soldering ability and/or a better adhesive ability
of the tin on the base material. However, the surface is
in both cases lightly oxidized or not protected against
further oxidation so that a permanent low contact
resistance even under mechanical stress is not
guaranteed.

 The basic purpose of the invention is to provide a
strip composite material of the mentioned type with an
oxide-free surface and which has a good wear and
corrosion resistance.

25 This purpose is surprisingly attained by embedding 1
to 50 At.-% carbon (C), preferably 6 to 30 At.-% C, in an
outer surface region of the tin coating up to a thickness
D of approximately 2 μm (At.-% = atomic weight-%).

30 The embedding of carbon into the Sn layer results in
an improvement of the friction behavior, namely, in plug
connectors, in the reduction of the plugging and pulling
force, in the improvement of the corrosion resistance, in
particular the resistance to fretting corrosion, and thus
in the guarantee of a constant contact transfer
35 resistance during the life of, for example, plug
connectors. The oil cannot be removed, for example,
through an ultrasound treatment in acetone. However,

there exist no oxidic binding structures of the main elements.

The base material consists preferably of copper or a copper alloy, of iron or an iron alloy, of nickel or a nickel alloy, of zinc or a zinc alloy.

A method for the manufacture of the composite material of the invention is characterized in such a manner that the tinned base material is pulled through a hot oil bath for a duration of 1 min. to 130 min., which oil bath contains an oil on a paraffin and/or ester and/or fatty acid base, both of a natural and also synthetic origin with common additives, and the temperature T of which oil bath lies above the melting point of the respective tinning. The hot oil bath contains preferably a paraffin oil or paraffin-based solvent raffinates and is free of chlorine or PCB. The temperature lies above the melting point of the respective tinning: in the case of pure tin thus preferably at 240°C, in the case of SnPb at 200°C, in the case of SnAgO, 5Sb1 at 250°C. The duration is preferably 2 min. to 4 min.

The intermetallic phase (IMP) is adjusted depending on the layer thickness and temperature / time treatment to 10% to 100% of the entire tin layer thickness. The Sn surface shows then a high-gloss surface, which is corrosion-resistant, in particular, however, friction-corrosion-resistant. The static contact resistance does not change with the oil treatment. The friction forces are reduced through this by 20% to 75%.

It is furthermore advisable to quench the composite material immediately after the oil treatment in a cold oil bath on a paraffin and/or ester and/or fatty acid base, both of a natural and also synthetic origin with the usual additives, at a temperature of 5°C to 50°C, in particular at 20°C to 30°C. The C content in the Sn layer is furthermore increased by this quenching. The

duration of the composite material in the cold oil bath is preferably 2 min. to 10 min.

An apparatus for carrying out this modification of the invention is characterized by the characteristics of Claims 10 to 14.

According to a further modification of the invention, oil on a paraffin and/or ester and/or fatty acid base, both of a natural and also synthetic origin with the usual additives, is sprayed directly after the tinning of the base material onto the still hot tin coating. The oil is hereby not too tightly "bound" to the tinning, however, compared with the non-treated tinning positive influences, in particular with respect to the friction corrosion, can be measured.

The invention will be discussed in greater detail in connection with the following exemplary embodiment:

The figure shows schematically the sequence of the heat treatment of tinned strips 1 in a hot oil 2 of a hot-oil part 3 with a subsequent quenching in cold oil 4 of a cold-oil part 5, whereby the strip 1 is guided cold from an unwinding device 6 (not illustrated in detail) through guide rollers 7 and a lock 8 into the hot oil bath 2 heated to 190°C to 270°C. The oil-bath temperature must thereby lie above the melting point of the respective tinning. When the strip 1 is inductively brought up to temperature and moves then into the oil bath 2, there exists the danger of the formation of decrosslinkings and of the "bone-shaped effect".

A smoke exhaust 9 is integrated at the highest point of the hot-oil part 3.

The strip 1 moves through a thermal lock 10 and around a guide roller 11 into a cooled oil bath 4 with a temperature of 5°C to 50°C, preferably 10°C to 30°C, for quenching without air supply. When emerging from the oil bath 4, the excessive oil is wiped off by exhaust nozzles 12 or squeezing rollers, and the strip 1, guided by a guide roller 13, is wound up (onto a winding-up device 14

not illustrated in detail). The hot oil 2 is circulated by a circulation system having an integrated heating device. The cold oil 4 is circulated by a further circulation system having an integrated return-cooling device. The drain 15 is used only for servicing purposes.

Numerical Example:

A CuSn6-bronze strip with the dimension 0.63 mm x 80 mm was hot-tinned with pure tin (layer thickness approximately 1.8 mm) and subsequently oil-treated in a bath of commercially available, paraffin-based solvent raffinate (the respective treatment parameters are listed in Column I of the following table).

I	II	III	IV
Treatment (A ^{1,)} = Quenching)	Layer Thickness RFA [μ m] Coul (VS/RS) (VS/RS)	C-content in At.-% 0 $\rightarrow$ 2 μ m Depth	Fretting Corrosion [m Ω /cycles]
Initial State	1.5/1.7 1.1/1.5	0.7% $\rightarrow$ 0%	1000/1250
195°C/1 min 195°C/4 min A ^{1,)}	1.5/1.7 0.8/1.3 1.5/1.8 0.8/0.7	6% $\rightarrow$ 0.8% 1% $\rightarrow$ 0.6%	1000/2080 1000/1850
250°C/4 min 250°C/4 min A ^{1,)}	1.4/1.8 n.n. ^{2,)} /0.2 1.4/1.8 n.n. ^{2,)} /n.n. ^{2,)}	10% $\rightarrow$ 0.1% 25.8% $\rightarrow$ 0.1%	3.8/5000 2.6/5000
	n.n. ^{2,)} = Cannot be proven		

Column II of the table lists the layer thickness on each of the front side (VS) and the back side (RS) of the strip. The layer thickness, which is measured by means of radiograph-fluorescence-analysis (RFA), is thereby the entire thickness of the free Sn layer and of the intermetallic phase (IMP), whereas the coulometrically measured layer thickness relates only to the free Sn layer. The difference thus results in the thickness of the IMP.

Column III of the table lists the C content, which is measured by means of auger-electron-spectroscopy (AES) and secondary-ion-mass-spectroscopy (sims).

Column IV of the table lists the fretting corrosion tendency, measured in accordance with the so-called "rider-on-flat" method (contact resistance in m Ω after n cycles at 1 N contact force and 25 μ m amplitude). Either the number of cycles is thereby disclosed, after which a contact resistance of 1000 m Ω is reached, or - if 1000 m Ω is not reached - the measuring is stopped after 5000 cycles.

Using the table, it is stated that through an oil treatment at 195°C compared with the initial state indeed a slight improvement with respect to the construction of the IMP and the fretting corrosion tendency is achieved, however, a significant shortening of the up to now common times for adjusting the IMP is achieved only through the oil treatment of the invention at 250°C (a free Sn layer can no longer be detected according to Column II).

The fretting corrosion tendency is at the same time considerably reduced with an increasing carbon content.



1. A strip composite material with a base material of metal or a metal alloy and with a surface coating of a pure tin or a tin alloy, which surface coating is applied galvanically or by melt tinning, whereby an intermetallic phase (IMP) is constructed between both materials, characterized in that 1 to 50 At.-% carbon (C) are embedded in an outer edge section of the tin coating up to a thickness D of approximately 2 μm .

2. The composite material according to Claim 1, characterized in that 6 to 30 At.-% C are embedded.

3. The composite material according to Claim 1 or 2, characterized in that the base material consists of copper or a copper alloy, of iron or an iron alloy, of nickel or a nickel alloy, of zinc or a zinc alloy.

4. A method for the manufacture of a strip composite material according to one or several of the Claims 1 to 3, characterized in that the base material is pulled through a hot oil bath for a duration of 1 min. to 130 min., which oil bath contains an oil on a paraffin and/or ester and/or fatty acid base, both of a natural and also synthetic origin with common additives, and the temperature T of which oil bath lies above the melting point of the respective tinning.

5. The method according to Claim 4, characterized in that the duration is 2 min. to 4 min.

6. The method according to Claim 4 or 5, characterized in that the composite material is quenched immediately following the oil treatment in a cold oil bath on a paraffin and/or ester and/or fatty acid base,



both of a natural and also synthetic origin with common additives, at a temperature of 5°C to 50°C.

5 7. The method according to Claim 6, characterized in that quenching takes place at a temperature of 10°C to 30°C.

10 8. The method according to Claim 6 or 7, characterized in that the duration of the composite material in the cold oil bath is 2 min. to 10 min.

15 9. The method for the manufacture of a strip composite material according to one or several of the Claims 1 to 3, characterized in that oil on a paraffin and/or ester and/or fatty acid base, both of a natural and also synthetic origin with the usual additives, is sprayed directly after the tinning of the base material onto the still hot tin coating.

20 10. An apparatus for carrying out the method according to one or several of the Claims 4 to 8, characterized in that it has an unwinding device (6), a hot-oil part (3), a thermal lock (10), a cold-oil part (5) and a winding-up device (14).

25 11. The apparatus according to Claim 10, characterized in that a lock (8) is connected in front of the hot-oil part (3).

30 12. The apparatus according to Claim 10 or 11, characterized in that a guide roller (11) is arranged in the cold-oil part (5).

35 13. The apparatus according to one or several of the Claims 10 to 12, characterized in that separate circulation systems are provided for each of the hot-oil part (3) and the cold-oil part (5).



14. The apparatus according to Claim 13,
characterized in that a return-cooling device is
integrated into the circulation system.