

CORROSION AND MOISTURE RESISTANT BONDING WIRE

The invention relates to an 8 to 80 μm thick wire comprising a copper core comprising: copper, nickel in an amount in the range of from 0.005 to 5 wt.-% (weight-%, % by weight), and, optionally, silver in an amount in the range of from 0.005 to 1 wt.-%, wherein all amounts in wt.-% are based on the total weight of the core; wherein the copper core has an average size of crystal grains in the range of from 1.5 to 30 μm . The invention further relates to a process for manufacturing such wire.

The use of bonding wires in electronics and microelectronics applications is well-known state of the art. While bonding wires were made from gold in the beginning, nowadays less expensive materials are used such as copper. While copper wire provides very good electric and thermal conductivity, bonding of copper wire has its challenges. Moreover, copper wires are susceptible to corrosion, and oxidation.

With respect to wire geometry, most common are bonding wires of circular cross-section and bonding ribbons which have a more or less rectangular cross-section. Both types of wire geometries have their advantages making them useful for specific applications.

Some recent developments were directed to bonding wires having a copper core. As core material, copper is chosen because of high electric conductivity. Different dopants to the copper material have been searched for in order to optimize the bonding properties. For example, US 7,952,028 B2 describes several different copper-based test wires with a large number of different dopants and concentrations.

Nevertheless, there is an ongoing need for further improving bonding wire technology with regard to the bonding wire itself and the bonding processes.

Accordingly, it is an object of the invention to provide improved bonding wires.

It is a further object of the invention to provide a bonding wire which exhibits excellent bondability with respect to a stitch bonding.

5 It is another object of the invention to provide a bonding wire which has improved reliability and improved resistance to corrosion and moisture.

It is a further object of the invention to provide a bonding wire which exhibits an improved reliability and bondability with respect to a ball bonding.

10 It is a further object of the invention to provide a bonding wire which exhibits an improved bonded ball roundness and concentricity with respect to ball-wedge bonding.

The wires of the invention have been found to solve at least the object of improved corrosion and moisture resistance. Further, a process for manufacturing these wires has
15 been found.

A contribution to the solution of the above objects is provided by the subject-matter of the category-forming claims. The dependent sub-claims of the category-forming claims represent preferred embodiments of the invention, the subject-matter of which also
20 makes a contribution to solving the objects mentioned above.

A first aspect of the invention is a wire comprising a core comprising or consisting of
(a) nickel in an amount in the range of from 0.005 to 5 wt.-%, preferably 0.1 to 0.6 wt.-% or even 0.45 to 0.55 wt.-%,
25 (b) optionally, silver in an amount in the range of from 0.005 to 1 wt.-%, preferably 0.1 to 0.6 wt.-% or even 0.45 to 0.55 wt.-%,
(c) copper in an amount in the range of from 94 wt.-% to 99.98 wt.-%, preferably 98.5 to 99.6 wt.-% or even 99.4 to 99.6 wt.-%, and
(d) 0 to 100 wt.-ppm (weight-ppm, ppm by weight) of further components,
30 wherein all amounts in wt.-% and wt.-ppm are based on the total weight of the core, wherein the core has an average size of crystal grains in the range of from 1.5 to 30 μm , the average size determined according to the line intercept method,

wherein the wire has an average diameter in the range of from 8 to 80 μm or even 12 to 55 μm .

The wire is preferably a bonding wire for bonding in microelectronics. The wire is preferably a one-piece object. Numerous shapes are known and appear useful for wires of the invention. Preferred shapes are – in cross-sectional view – round, ellipsoid and rectangular shapes.

The average diameter is obtained by the “sizing method”. According to this method the physical weight of the wire for a defined length is determined. Based on this weight, the diameter of the wire is calculated using the density of the wire material (density of copper: $\rho_{\text{Cu}} = 8.92 \text{ g/cm}^3$). The average diameter is calculated as arithmetic mean of five measurements on five cuts of a particular wire.

For the invention, the term “bonding wire” comprises all shapes of cross-sections and all usual wire diameters, though bonding wires with circular cross-section and thin diameters are preferred.

The line intercept method for determining the average size of crystal grains is a standard metallographic practice. There, a wire is cut perpendicular to the direction of the wire and the cross-section generated thereby is etched. The size of a crystal grain in the present context is defined as the longest of all sections of straight lines which can be passed through the grain. The average size of crystal grains is the arithmetic mean of at least seven measurements of crystal grains in the core/bulk material. The testing is performed according to ASTM E112-96 standard, section 16.3, page 13.

As already mentioned, the core of the wire comprises (a) 0.005 to 5 wt.-% of nickel and (c) 94 to 99.98 wt.-% of copper. The core of the wire may or may not comprise component (b), i.e. silver. If the core of the wire comprises silver, the silver amount is in the range of from 0.005 to 1 wt.-%.

The core of the wire of the invention comprises (d) 0 to 100 wt.-ppm of further components. The low amount of these further components ensures a good reproducibility of the wire properties. In the present context, the further components, often also referred as "inevitable impurities", are minor amounts of chemical elements and/or compounds which originate from impurities present in the raw materials used or from the wire manufacturing process. Examples of such further components are: Mn, Pt, Cr, Ca, Ce, Mg, La, Al, B, Zr, Ti, S, Fe.

In other words, the core comprises or consists of

(a) nickel in an amount in the range of from 0.005 to 5 wt.-%, preferably 0.1 to 0.6 wt.-% or even 0.45 to 0.55 wt.-%,

(b) silver in an amount in the range of from 0.005 to 1 wt.-%, preferably 0.1 to 0.6 wt.-% or even 0.45 to 0.55 wt.-%,

(c) copper in an amount in the range of from 94 to 99.98 wt.-%, preferably 98.5 to 99.6 wt.-% or even 99.4 to 99.6 wt.-%, and

(d) 0 to 100 wt.-ppm of further components,
or

(a) nickel in an amount in the range of from 0.005 to 5 wt.-%, preferably 0.1 to 0.6 wt.-% or even 0.45 to 0.55 wt.-%,

(b) no silver,

(c) copper in an amount in the range of from 94 to 99.98 wt.-%, preferably 98.5 to 99.6 wt.-% or even 99.4 to 99.6 wt.-%, and

(d) 0 to 100 wt.-ppm of further components,

wherein all amounts in wt.-% and wt.-ppm are based on the total weight of the core.

In line with the aforementioned, an embodiment of the invention is a wire comprising (a) nickel, (b) optionally, silver, and (c) copper, as disclosed above. Further components present in the core are usually not added separately. The presence of the further components originates from impurities present in one or more of the nickel, silver and copper.

In an embodiment, the core of the wire of the invention comprises less than the following amounts of further components:

(i) Mn in <15 wt.-ppm;

(ii) any one of: Pt, Cr, Ca, Ce, Mg, La, Al, B, Zr, Ti in <2 wt.-ppm each;

5 (iii) any one of S, Fe in <10 wt.-ppm each.

Yet more preferred at least two of the aforementioned limits are met by the material forming the core, most preferred all limits are met by the material forming the core.

10 In an embodiment, the wire core comprises elemental phosphorus as a dopant in an amount in the range of from 40 to 80 wt.-ppm, based on the total weight of the core.

The core of the wire in the present context is defined as a homogenous region of bulk material. Since any bulk material always has a surface region which might exhibit
15 different properties to some extent, the properties of the core of the wire are understood as properties of the homogeneous region of bulk material. The surface of the bulk material region can differ in terms of morphology, composition (e.g. oxygen content) and other features. The surface can be an outer surface of the wire core. In an alternative, it can be an interface region between the wire core and a coating layer superimposed on
20 the wire core.

The term "superimposed" in the context of the invention is used to describe the relative position of a first item, e.g. a copper core, with respect to a second item, e.g. a coating layer. "Superimposed" characterizes, that further items, such as an intermediate layer,
25 can – but no need to be arranged between the first and the second item. Preferably, the second item is at least partially superimposed over the first item, e.g. for at least 30 %, 50 %, 70 % or for at least 90 %, each with respect to the total surface of the first item. Most preferably, the second item is completely superimposed over the first item.

30 The term "intermediate layer" in the context of this invention refers to a region of the wire between the core and the coating layer. In this region, a combination of materials of both, the core and the coating layer, is present.

The term "thickness" in the context of this invention is used to define the size of a layer in perpendicular direction to the longitudinal axis of the core, which layer is at least partially superimposed over the surface of the core.

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In an embodiment, the ratio between the diameter of the core and the average size of crystal grains in the core is in the range of from 2 to 14 or even 2 to 7.

In an embodiment, the average diameter of the wire is in the range of from 15 to 28 μm .

10 In this case, the average size of crystal grains in the core is preferably in the range of from 1.5 to 6 μm .

In another embodiment, the average diameter of the wire is in the range of from > 28 to 38 μm . In this case, the average size of crystal grains in the core is preferably in the
15 range of from 2 to 10 μm .

In another embodiment, the average diameter of the wire is in the range of from > 38 to 50 μm . In this case, the average size of crystal grains in the core is preferably in the
20 range of from 5 to 15 μm .

In another embodiment, the average diameter of the wire is in the range of from > 50 to 80 μm . In this case, the average size of crystal grains in the core is preferably in the
range of from 7 to 30 μm .

25 In an embodiment, the core has a surface, wherein a coating layer is superimposed over the surface of the core.

In an embodiment, the mass of the coating layer is not more than 2.5 wt.-%, preferably 2 wt.-% or less, each with respect to the total mass of the core. When a coating layer is
30 present, it often has a minimum mass of 0.1 wt.-% or more or 0.5 wt.-% or more, each with respect to the total mass of the core. Applying a low amount of material as coating layer preserves the characteristics which are defined by the material of the core of the

wire. On the other hand, the coating layer awards particular characteristics to the wire surface such as being inert against environment, resistance to corrosion, improved bondability, etc. For example, the thickness of the coating layer is in the range of from 60 to 70 nm for a wire of an average diameter of 18 μm . For a wire having an average diameter of 25 μm , the coating layer may have a thickness in the range of from 90 to 100 nm, for example.

In an embodiment, the coating layer is made of an element selected from the group consisting of palladium, platinum and silver. The coating layer can be a monolayer of one of said elements. In another embodiment, the coating layer can be a multilayer of a number of super-positioned adjacent layers, wherein each layer is made of one element selected from the group consisting of palladium, platinum and silver. Each layer which is part of the coating layer is deposited individually from one of the aforementioned pure metal elements. Common techniques for deposition of these elements on the core are plating, such as electroplating and electroless plating, deposition of the material from the gas phase such as sputtering, ion plating, vacuum evaporation and physical vapor deposition, and deposition of the material from the melt.

In an embodiment, a further coating layer is superimposed over the coating layer. In an embodiment, the mass of the further coating layer is not more than 0.2 wt.-%, preferably not more than 0.1 wt.-%, each with respect to the total mass of the core.

For example, the thickness of the further coating layer lies in the range of from 2 to 4 nm for a wire having an average diameter of 18 μm . For a wire with an average diameter of 25 μm , the further coating layer may have a thickness of 3.5 to 5.5 nm, for example.

In an embodiment, the further coating layer is a gold layer.

In an embodiment, the wire of the invention is characterized at least by one of the following features:

α) The corrosion resistance has a value of at most 0% bonded ball lift; see "Test method G" as described below.

β) The moisture resistance has a value of at most 0% bonded ball lift; see "Test method I" as described below.

5 γ) The hardness of the wire core is not more than 120 HV, preferably not more than 115 HV, or not more than 110 HV; see "Test method J" as described below.

δ) The process window area for stitch bonding has a value of at least 40 $\mu\text{m}\cdot\text{g}$, or of at least 90 $\mu\text{m}\cdot\text{g}$, or of at least 120 $\mu\text{m}\cdot\text{g}$, each provided the wire has an average diameter of 18 μm ; see section "Test method C" as described below.

10 ϵ) The resistivity of the wire is not more than 1.80 $\mu\Omega\cdot\text{cm}$.

ζ) The average bonded ball roundness has a value of at most 0.0025 μm , or of at most 0.002 μm , or of at most 0.0018 μm each provided the wire has an average diameter of 18 μm ; see section "Test method E" as described below.

15 η) The average bonded ball concentricity has a value of at most 0.00056 μm , or of at most 0.0005 μm , or of at most 0.0004 μm each provided the wire has an average diameter of 18 μm ; see section "Test method E" as described below.

A second aspect of the invention is a process for manufacturing a wire in any of its embodiments disclosed above. In its most general embodiment the process comprises

20 at least the process steps of

(1) providing a precursor item comprising or consisting of:

(a) nickel in an amount in the range of from 0.005 to 5 wt.-%, preferably 0.1 to 0.6 wt.-% or even 0.45 to 0.55 wt.-%,

25 (b) optionally, silver in an amount in the range of from 0.005 to 1 wt.-%, preferably 0.1 to 0.6 wt.-% or even 0.45 to 0.55 wt.-%,

(c) copper in an amount in the range of from 94 wt.-% to 99.98 wt.-%, preferably 98.5 to 99.6 wt.-% or even 99.4 to 99.6 wt.-%, and

(d) 0 to 100 wt.-ppm of further components,

30 wherein all amounts in wt.-% and wt.-ppm are based on the total weight of the precursor item,

(2) elongating the precursor item to form a wire precursor, until the desired diameter of the wire core is obtained; and

(3) annealing the elongated wire precursor obtained after completion of process step (2).

A precursor item as provided in process step (1) can be obtained by alloying and/or
5 doping copper with the desired amount of nickel and, optionally, silver. Alloying and
doping is realized by producing a melt of said components and copper and cooling the
melt to form a homogeneous piece of copper based precursor item. Typically, such
precursor item is in the form of a rod having a diameter of, for example, 2 to 25 mm and
a length of, for example, 5 to 100 m. Such rod can be made by casting a copper alloy
10 melt comprising or consisting of (a) nickel in an amount in the range of from 0.005 to 5
wt.-%, (b) optionally, silver in an amount in the range of from 0.005 to 1 wt.-%, (c)
copper in an amount in the range of from 94 to 99.98 wt.-%, and (d) 0 to 100 wt.-ppm of
further components in an appropriate mold of room temperature, followed by cooling
and solidifying, wherein all amounts in wt.-% and wt.-ppm are based on the total weight
15 of the copper alloy melt. The copper alloy itself can be prepared by conventional
processes known to the person skilled in the art of metal alloys, for example, by melting
together the copper, the nickel and, optionally, the silver in the desired ratio. In doing so,
it is possible to make use of conventional copper-nickel and copper-silver master alloys.
The melting process can for example be performed making use of an induction furnace
20 and it is expedient to work under vacuum or under an inert gas atmosphere. The
materials used can have a purity grade of, for example, 99.99 wt.-% and above.

If one or more coating layers are present on the wire as disclosed for some of the
embodiments of the first aspect of the invention, these coating layers are preferably
25 applied to the wire precursor. The skilled person knows how to calculate the thickness
of such coating layers on a precursor item to obtain the coating layers in the thickness
disclosed for the embodiments of the wire, i.e. after elongating the precursor item with
the one or more coating layers to the wire precursor. As already disclosed above,
numerous techniques for forming a coating layer of a material according to the
30 embodiments on a copper or copper alloy surface are known. Preferred techniques are
plating, such as electroplating and electroless plating, deposition of the material from

the gas phase such as sputtering, ion plating, vacuum evaporation and physical vapor deposition, and deposition of the material from the melt.

In order to superimpose a single- or multi-layer metal coating to the wire core as disclosed for some of the embodiments of the first aspect of the invention, it is expedient to interrupt process step (2) once a certain precursor diameter in the range of, for example, 80 to 200 μm is reached. Then the single- or multi-layer metal coating may be applied, for example, by one or more electroplating process steps. Thereafter process step (2) is continued until the desired and final diameter of the wire core is obtained.

In process step (2) the precursor item is elongated to form a wire precursor, until the desired diameter of the wire core is obtained. Numerous techniques are known to elongate a precursor item to form a wire precursor are known and appear useful in the context of the invention. Preferred techniques are rolling, swaging, die drawing or the like, of which die drawing is particularly preferred. In the latter case the precursor item is drawn in several process steps until the desired and final diameter of the wire core is reached.

The desired and final diameter of the wire core may be in the range of from 8 to 80 μm or, preferably, in the range of from 12 to 55 μm . Such wire die drawing process is well known to the person skilled in the art.

Conventional tungsten carbide and diamond drawing dies may be employed and conventional drawing lubricants may be employed to support the drawing. For example, the precursor item may be drawn in 8 major stages and each stage with 15 to 25 process steps, wherein in each drawing process step an elongation of the precursor item in the range of from 6 to 18 % in length is performed. The % of elongation may be same or different for each drawing process step.

In process step (3) the elongated wire precursor obtained after completion of process step (2), is annealed, preferably in a tubular oven. Preferably, the annealing is strand

annealing (final annealing), which is a continuous process allowing for a fast production of the wire with high reproducibility. Strand annealing means that the annealing is done dynamically while the wire precursor is moved through a preferably tubular annealing oven and spooled onto a reel after having left the oven. The annealing is performed at an object temperature in the range of, for example, 440 to 700 °C for 0.1 to 0.4 seconds, preferably 470 to 650 °C for 0.1 to 0.3 seconds; these temperature/time conditions allow for achieving or adjusting the desired average crystal grain size of the wire core.

The annealing is typically performed by pulling the elongated wire precursor through a conventional annealing oven, typically in the form of a cylindrical tube of a given length and with a defined temperature profile at a given annealing speed which may be chosen in the range of, for example, from 4 to 30 meters/minute, or from 14 to 16 meters/minute. In so doing the annealing time/object temperature parameters can be defined and set.

With respect to an embodiment of the invention, it was found that annealing at a temperature below the temperature of maximum elongation can result in beneficial wire properties as the wire morphology can be influenced in a positive way. Further, it has been found that selecting the annealing temperature to be higher than the temperature of maximum elongation while maintaining the annealing time constant, is of further advantage. For example, this manufacturing principle can be used to adjust the average grain size of the wire, e.g. to larger average grain sizes. By this adjustment, other properties like e.g. wire hardness, ball-bonding behavior etc. can be influenced in a positive manner.

Hence, in an embodiment, annealing is performed at a temperature above the temperature of maximum elongation wherein the elongation value of the wire after annealing is not more than 98% of the maximum elongation value. For example, process step (3) may be performed at a temperature which is at least 10 °C, preferably at least 50 °C, or at least 80 °C higher than the temperature of maximum elongation $T_{\Delta L(max)}$. Often, the temperature in process step (3) is not more than 200 °C higher than

$T_{\Delta L(max)}$. The temperature of maximum elongation $T_{\Delta L(max)}$ is determined by testing the elongation at break of a specimen (wire) at different temperatures. The data points are collected in a graph, showing the elongation (in %) as a function of temperature ($^{\circ}C$). The resulting graph is often referred to as an “annealing curve”. In the case of copper based wires, a temperature is observed where the elongation (in %) reaches a maximum. This is the temperature of maximum elongation $T_{\Delta L(max)}$. An example is shown in Figure 1, which shows an exemplary annealing curve of a nickel-alloyed 18 μm copper wire according to sample 3 (Table 1). The annealing temperature is the variable parameter of the x-axis. The graph shows the measured values of the break load (BL, in grams) and the elongation (EL, in %) of the wire. The elongation was determined by tensile testing. Elongation measurements exhibited a typical local maximum value of about 10 % in the displayed example, which was achieved at an annealing temperature of around 470 $^{\circ}C$. If the wire according to sample 3 was not annealed at this temperature of maximum elongation, but at 560 $^{\circ}C$, which was 90 $^{\circ}C$ above the temperature of the maximum elongation the result is an elongation value of about 9.8%, which is more than 2% below the maximum elongation value.

The annealing may be performed in an inert or reducing atmosphere. Numerous types of inert atmospheres as well as reducing atmospheres are known in the art and are used for purging the annealing oven which is typically a tubular annealing oven. Of the known inert atmospheres, nitrogen is preferred. Of the known reducing atmospheres, hydrogen is preferred. Another preferred reducing atmosphere is a mixture of hydrogen and nitrogen. Preferred mixtures of hydrogen and nitrogen are 90 to 98 vol.-% nitrogen and, accordingly, 2 to 10 vol.-% hydrogen, wherein the vol.-% total 100 vol.-%.

Preferred mixtures of nitrogen/hydrogen are equal to 93/7, 95/5 and 97/3 vol.-%/vol.-%, each based on the total volume of the mixture. Applying reducing atmospheres in annealing is particularly preferred, if some parts of the surface of the wire are sensitive to oxidation by oxygen of the air, e.g. if copper of the wire is exposed to its surface. Purging with said types of inert or reducing gas is preferably performed at a gas exchange rate (= gas flow rate [liter/min] : inner oven volume [liter]) lying in the range of 43 to 125 min^{-1} , more preferably 43 to 75 min^{-1} , most preferably 50 to 63 min^{-1} .

It is believed that the unique combination of the composition of the precursor item material (which is the same as that of the finished wire core) and the process parameters prevailing during process step (3) is essential to obtain the wire of the invention. A preferred combination of said process parameters is: object temperature of 500 to 650 °C for 0.1 to 0.3 seconds, preferably in further combination with the use of 90-98 vol.-% nitrogen/2-10 vol.-% hydrogen mixtures as purging gas at a gas exchange rate in the range of 50 to 63 min⁻¹.

After completion of process step (3) the wire of the invention is finished. In order to fully benefit from its properties, it is expedient to either use it immediately for wire bonding applications, i.e. without delay, for example, within no longer than 7 days after completion of process step (3). Alternatively, in order to keep the wire's wide wire bonding process window property and in order to prevent it from oxidative or other chemical attack, the finished wire is typically spooled and vacuum sealed immediately after completion of process step (3), i.e. without delay, for example, within <1 to 5 hours after completion of process step (3) and then stored for further use as bonding wire. Storage in vacuum sealed condition should not exceed 6 months. After opening the vacuum seal the wire should be used for wire bonding within no longer than 7 days.

It is preferred that all process steps (1) to (3) as well as spooling and vacuum sealing are carried out under clean room conditions (US FED STD 209E cleanroom standards, 1k standard).

A third aspect of the invention is a wire obtainable by a process according to the second aspect of the invention or of an embodiment thereof. It has been found that said wire is well suited for use as a bonding wire in wire bonding applications. Wire bonding technique is well known to the skilled person. In the course of wire bonding it is typical that a ball bond (1st bond) and a stitch bond (2nd bond, wedge bond) are formed. During bond forming a certain force (typically measured in grams) is applied, supported by application of scrub amplitude (typically measured in µm). The mathematical product of the difference between the upper and the lower limits of the applied force and the

difference between the upper and the lower limits of the applied scrub amplitude in a wire bonding process defines the wire bonding process window:

$$(Upper\ limit\ of\ applied\ force - Lower\ limit\ of\ applied\ force) \cdot (Upper\ limit\ of\ applied\ scrub\ amplitude - Lower\ limit\ of\ applied\ scrub\ amplitude) = Wire\ bonding\ process\ window.$$

The wire bonding process window defines the area of force/scrub amplitude combinations which allow formation of a wire bond that meets specifications, i.e. which passes the conventional tests like conventional pull tests, ball shear test and ball pull test to name only few.

For industrial applications it is desirable to have a wide wire bonding process window (force in g versus scrub amplitude in μm) for reasons of wire bonding process robustness. The wire of the invention exhibits a considerably wide wire bonding process window. For example, a wire of the invention 18 μm in diameter exhibits a wire bonding process window in the range of, for example, 40 to 120 $\mu\text{m}\cdot\text{g}$ for stitch bonding.

The following non-limiting examples illustrate the invention.

20 Examples

Test methods A. to J.

All tests and measurements were conducted at $T = 20\text{ }^{\circ}\text{C}$ and a relative humidity $\text{RH} = 50\%$.

25 A. Average size of crystal grains by line intercept method:
The size of crystal grains was determined using a standard metallographic technique, ASTM E112-96, section 16.3, page 13. A sample of the wire core was cross-sectioned and then etched. In the present case, a solution of 2 g FeCl_3 and 6 ml concentrated HCl in 200 ml deionized water was used for the etching. The crystal grain size was
30 determined according to the line intercept principle. The size of a crystal grain in the present context was defined as the longest of all sections of straight lines which passed

through the grain. The measured average size of crystal grains was the arithmetic mean of at least seven measurements of crystal grains in the core material.

B. Elongation (EL):

- 5 The tensile properties of the wires were tested using an Instron-5300 instrument. The wires were tested at 1 inch/min speed, for 10 inch gauge length. The load and elongation on fracture (break) were acquired as per ASTM standard F219-96. The elongation was the difference in the length of the wire before and after tensile testing ($\Delta L/L$), calculated from the recorded load versus extension tensile plot.

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C. Stitch bonding process window area:

- Measurements of bonding process window area were done by standard procedure. The test wires were bonded using a KNS-iConn bonder tool (Kulicke & Soffa Industries Inc, Fort Washington, PA, USA). The 2nd bond (stitch bond) process window area is the
 15 product of the difference between the upper and the lower limits of the force used in the bonding and the difference between the upper and the lower limits of the applied scrub amplitude, wherein the resulting bond has to meet certain pull test specifications, e.g. a pull force of 2.5 grams, no non-stick on lead etc.. The process window values were based on a wire having an average diameter of 18 μm , wherein the lead finger to which
 20 the wire was bonded consisted of silver.

The four corners of the process window were derived by overcoming the two main failure modes:

- (1) supply of too low force and scrub amplitude lead to non-stick on lead (NSOL) of the
 25 wire, and
 (2) supply of too high force and scrub amplitude lead to short tail (SHTL).

D. Free air ball (FAB):

- FAB was evaluated by performing conventional electric flame-off (EFO) firing in 2
 30 different modes; (a) standard firing - single step and (b) advanced firing – two steps, see the following table:

	Steps	EFO current in mA	Time in μ s
Standard Firing Mode	1	50	195
Advanced Firing Mode	1	100	62.5
	2	50	62.5

It was worked according to the procedures described in the KNS Process User Guide for Free Air Ball (Kulicke & Soffa Industries Inc, Fort Washington, PA, USA, 2002, 31 May 2009). The FAB diameter was measured using optical microscope at 200X to 500X magnification in μ m scale. Morphology of the FAB was observed using scanning electron microscope (SEM). The shape and symmetry of the molten drop of wire material hanging at the end of the wire prior to stitch bonding was evaluated.

Evaluation of performance of FAB formation:

+, molten drop of wire solidifies, but the ball size is smaller than the specification and/or pointed

++, molten drop of wire solidifies with spherical shape, but the ball size is out of specification and/or tilted

+++, molten drop of wire solidifies with spherical shape and within the specification, but slightly tilted

++++, molten drop of the wire solidifies with spherical and axi-symmetrical ball like shape

E. Average Bonded Ball Roundness and Concentricity:

Bonded ball (1st bond) morphologies were quantified by measuring the average roundness and concentricity. The wires were bonded using standard or advanced firing mode. The 4N bare copper and nickel alloyed copper wires were bonded using standard firing mode, while silver-nickel alloyed copper wires were bonded using advanced firing mode.

Bonded ball was observed in high power Nikon microscope MM40 at 500X magnification. E-max software version 5.3 interlinked to microscope predicted a theoretical circle by least square method for 16 measured edge points. The deviation of each edge to the theoretical circle radii were found. The difference between maximum and minimum deviation value was defined as DevE, the average roundness of a bonded ball. A well rounded ball showed 0.001 μm and worst ball revealed 0.003 μm average roundness.

In case of average bonded ball concentricity, 12 edges were marked along the outer circle. E-max software predicted a theoretical circle by least square method and found the centre of the outer circle. Similarly, it predicted inner circle and its centre. The difference in the centre between outer and inner circle for both X and Y direction were calculated, from which the concentricity was calculated as $\Delta C = \sqrt{\Delta X^2 + \Delta Y^2}$. A well concentric bonded ball showed 0.0001 μm and worst ball revealed of 0.0009 μm .

F. Salt-solution soaking test of continuous cast rods:

Continuous cast 8 mm rods were parted for 10 mm length and soaked in salt-solution at 85 $^{\circ}\text{C}$ for 4 days, washed using DI water and later with acetone. The salt-solution contained 20 wt.-% NaCl dissolved in de-ionised (DI) water. The surface discoloration of the rods was observed under lower power scope (Stereoscope - SZX16) at 10 to 100X magnification. Rod surface that transformed from original copper rose to dark black indicated severe crevice corrosion. SEM-EDX on the dark black surface revealed peaks of chlorine, oxygen and copper.

Evaluation:

+, 100% cast rod surface transformed from original copper rose to dark black color, indication of severe crevice corrosion

++, < 70% cast rod surface transformed from original copper rose to black color, indication of crevice corrosion

+++, < 40% cast rod surface transformed from original copper rose to black color, indication of mild crevice corrosion

++++, < 10% cast rod surface transformed from original copper rose to dark black color, indication of less significance or absence of crevice corrosion

G. Salt-solution soaking test of bonded balls:

- 5 The wires were ball bonded to Al-0.5wt.-%Cu bond pads. The test devices with the so-bonded wires were soaked in salt-solution at 25 °C for 2, 4, 6, 8 and 10 minutes, washed with DI water and later with acetone. The salt-solution contained 30 wt.-ppm NaCl in de-ionised (DI) water. The number of lifted balls were examined under lower power scope (Stereoscope - SZX16) at 10 to 100X magnification. Observation of a
10 higher number of lifted balls indicated severe interfacial galvanic corrosion.

H. Moisture resistance test of continuous cast rods:

- Continuous cast 8 mm rods were parted for 10mm length and stored at 130 °C temperature, 85 % relative humidity (RH) for 4 days in highly accelerated stress test
15 (HAST) chamber. The HAST tested samples were examined for surface discoloration under low power scope (Stereoscope - SZX16) at 10 to 100X magnification. Similar to salt-solution soaking test, rod surface that transformed from original copper rose to dark black indicated severe crevice corrosion. SEM-EDX on the dark black surface revealed
20 peaks of oxygen and copper.

Evaluation:

- +, 100% cast rod surface transformed from original copper rose to dark black color, indication of severe crevice corrosion
++ , < 70% cast rod surface transformed from original copper rose to black color,
25 indication of crevice corrosion
+++, < 40% cast rod surface transformed from original copper rose to black color, indication of mild crevice corrosion
++++, < 10% cast rod surface transformed from original copper rose to dark black color, indication of less significance or absence of crevice corrosion
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I. Moisture resistance test of bonded balls:

The wires were ball bonded to Al-0.5wt.-%Cu bond pads. The test devices with the so-bonded wires were stored at 130 °C temperature, 85 % relative humidity (RH) for 20 hours in highly accelerated stress test (HAST) chamber and later examined for number of lifted balls under lower scope (Stereoscope - SZX16) at 10 to 100X magnification. Observation of a higher number of lifted balls indicated severe interfacial galvanic corrosion.

J. Vickers Hardness:

The hardness was measured using a Fischer scope H110C testing equipment with a Vickers indenter. A force of 10 mN was applied to a test specimen of wire for a dwell time of 5 s. The testing was performed on the center of the annealed wire core.

Examples 1-10

A quantity of copper material of at least 99.99 % purity ("4N-copper") was melt in a crucible. A small amount of master alloy was added to the copper melt and uniform distribution of the added component was ascertained by stirring. The following master alloys were used.

Name of Master Alloy	Composition	
Cu-5wt.-%Ni	95 wt.-% Cu	5 wt.-% Ni
Cu-0.5wt.-%P	99.5 wt.-% Cu	0.5 wt.-% P
Cu-15wt.-%Ag	85 wt.-% Cu	15 wt.-% Ag

For the alloys of Tables 1 and 2 the corresponding combination of the master alloys Cu-5wt.-%Ni, Cu-15wt.-%Ag and Cu-0.5wt.-%P were added. Then wire precursors in the form of 8 mm rods were continuous cast from the melt.

The 8 mm rods were drawn in 6 major drawing stages with 22 process steps in each stage to form a wire of circular shape with an average diameter of 18 μm , wherein an elongation of the prefab

cursor of from 6 to 18 % in length was performed in each process step. In the examples presented herein, 17% elongation was practised for stage 1, 11% elongation was practised for stage 2 to stage 5 and 8% elongation was practised for stage 6. A slipping agent was employed during drawing.

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By means of this procedure, samples of copper-nickel and copper-nickel-silver alloy wires and of one comparative wire (Ref) were manufactured.

The chemical composition of the copper, copper-nickel and copper-nickel-silver alloy wires was controlled by ICP (inductively coupled plasma) analysis using a Perkin Elmer ICP-OES 7100DV model. The wires were dissolved in concentrated nitric acid and the solution was used for the ICP analysis.

Table 1 shows the composition of samples 1 to 6 of inventive copper-nickel alloy wires of 18 μm average diameter. The nickel content of the wires varied as indicated as did the amount of phosphorus. A comparative wire (Ref) consisted of 4N-copper.

Table 1: Chemical composition of copper and copper-nickel alloy wires, average diameter 18 μm , values in wt.-ppm

Sample	Ni	Ag	P	Pd	S	Fe	Mn
4N Cu (Ref)	5	12	1.1	1.2	1.8	1.9	0.2
1	50	12	1.1	1.2	1.8	1.9	0.2
2	500	12	1.1	1.2	1.8	1.9	0.2
3	5000	12	1.1	1.2	1.8	1.9	0.2
4	10000	12	1.1	1.2	1.8	1.9	0.2
5	50000	12	1.1	1.2	1.8	1.9	0.2
6	5000	12	50	1.2	1.8	1.9	0.2

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Table 2 shows the composition of sample wires 7 to 10 each of which having 18 μm average diameter. The silver, nickel and phosphorus content of the wires varied as indicated. A comparative wire (Ref) consisted of 4N-copper.

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Table 2: Chemical composition of copper and copper-nickel-silver alloy wires, average diameter 18 μm , values in wt.-ppm

Sample	Ni	Ag	P	Pd	S	Fe	Mn
4N Cu (Ref)	5	12	1.1	1.2	1.8	1.9	0.2
7	1000	1000	1.1	1.2	1.8	1.9	0.2
8	1000	5000	1.1	1.2	1.8	1.9	0.2
9	5000	1000	1.1	1.2	1.8	1.9	0.2
10	2500	2500	50	1.2	1.8	1.9	0.2

The wires were annealed in a final annealing process step. The annealing was performed dynamically as strand annealing, by running the wires through a tubular annealing oven of 30 cm length and an annealing temperature of 560°C (wires 1-6) or 650 °C (wires 7-10) with a speed of 1m/s. After leaving the oven the wires were spooled on a reel for packaging.

- 10 In the present examples the annealing time was the exposure time of a given piece of the moving wire within the heated oven, which was 0.3 s. Within the oven zone, a constant temperature was adjusted.

- 15 The average grain sizes of wire samples 1 to 10 were measured. The result was in the range of 3 μm to 6 μm for samples 1 to 6 and in the range of 1.5 μm to 6 μm for samples 7 to 10.

Table 3 below shows test results obtained with the 8 mm rods and the bonded wires of samples 1 to 6.

Table 3

		Samples						
		4N Cu (Ref)	1	2	3	4	5	6
Corrosion resistance test	Salt-solution soaked 8 mm rods	++	++	+++	++++	++++	++++	++++
	Salt-solution soaked bonded balls (% bonded ball lift)	8.5	8	5	0	0	0	0
Moisture resistance test	8 mm rods	++	++	+++	++++	++++	++++	++++
	Bonded balls (% bonded ball lift)	12	9.5	7	0	0	0	0
FAB	Performance of FAB formation	++++	++++	++++	++++	+++	+++	+++
Bonded ball	Average Roundness (μm)	0.0024	0.0024	0.0024	0.0025	0.0022	0.0022	0.0025
	Average Concentricity (μm)	0.00056	0.00056	0.00056	0.00056	0.00054	0.00054	0.00056
2nd bond process	Scrub amplitude (μm)	2-4	2-4	2-4	2-5	2-4	2-4	2-4
	Force (g)	80-100	80-110	80-110	80-110	80-110	80-110	80-110
	Window ($\mu\text{m}\cdot\text{g}$)	40	60	60	90	60	60	60

Table 4 below shows test results obtained with the 8 mm rods and the bonded wires of
5 samples 7 to 10.

Table 4

	Wire sample	4N Cu (Ref)	7	8	9	10
Corrosion resistance test	Salt-solution soaked 8mm rods	++	+++	++++	++++	++++
	Salt-solution soaked bonded balls (% bonded ball lift)	8.5	4	0	0	0
Moisture resistance test	8 mm rods	++	+++	++++	++++	++++
	Bonded balls (% bonded ball lift)	12	6	0	0	0
FAB	Performance of FAB formation	++++	+++	+++	+++	+++
Bonded ball	Average Roundness (μm)	0.0024	0.0018	0.0018	0.0018	0.0018
	Average Concentricity (μm)	0.00056	0.0004	0.0004	0.0004	0.0004
2nd bond process	Scrub amplitude (μm)	2-4	2-4	2-5	2-5	2-5
	Force (g)	80-100	80-110	80-110	80-110	80-110
	Window ($\mu\text{m}\cdot\text{g}$)	40	60	90	90	90

Wires 1-6 and 7-10 resulted in process windows which were well suited for industrial application. A significant improvement of the corrosion and moisture resistance of the cast rods and bonded balls was observed at least with a nickel content in a range of 0.5 wt.-% to 5 wt.-% or with a combination of silver in a range of 0.1 to 0.5 wt.-% and nickel in a range of 0.1 to 0.5 wt.-%.

CLAIMS

1. A wire comprising a core comprising or consisting of
 - (a) nickel in an amount in the range of from 0.005 to 5 wt.-%,
 - 5 (b) optionally, silver in an amount in the range of from 0.005 to 1 wt.-%,
 - (c) copper in an amount in the range of from 94 wt.-% to 99.98 wt.-%, and
 - (d) 0 to 100 wt.-ppm of further components,wherein all amounts in wt.-% and wt.-ppm are based on the total weight of the core,
10 wherein the core has an average size of crystal grains in the range of from 1.5 to 30 μm , the average size determined according to the line intercept method, wherein the wire has an average diameter in the range of from 8 to 80 μm .
2. The wire of claim 1,
15 wherein
the average diameter is in the range of from 12 to 55 μm .
3. The wire of claim 1 or 2,
wherein
20 the core has a surface which is an outer surface or wherein a coating layer is superimposed over the surface of the core.
4. The wire of claim 3,
wherein
25 the mass of the coating layer is not more than 2.5 wt.-%, with respect to the total mass of the core.
5. The wire of claim 3 or 4,
wherein
30 the coating layer is a monolayer of palladium, platinum or silver or a multilayer of a number of super-positioned adjacent layers, each layer being made of one element selected from the group consisting of palladium, platinum and silver.

6. The wire of claim 3, 4 or 5,
wherein
a further coating layer is superimposed over the coating layer.
- 5 7. The wire of claim 6,
wherein
the further coating layer is a gold layer.
- 10 8. The wire of any one of the preceding claims,
wherein
the wire core comprises elemental phosphorus as a dopant in an amount in the
range of from 40 to 80 wt.-ppm, based on the total weight of the core.
- 15 9. The wire of any one of the preceding claims,
wherein
the ratio between the diameter of the core and the average size of crystal grains in
the core is in the range of from 2 to 14.
- 20 10. The wire of any one of the preceding claims,
characterized at least by one of the following features:
- α) The corrosion resistance has a value of at most 0% bonded ball lift;
 β) The moisture resistance has a value of at most 0% bonded ball lift;
 γ) The hardness of the wire core is not more than 120 HV;
25 δ) The process window area for stitch bonding has a value of at least 40 $\mu\text{m}\cdot\text{g}$,
provided the wire has an average diameter of 18 μm ;
 ϵ) The resistivity of the wire is not more than 1.80 $\mu\Omega\cdot\text{cm}$;
 ζ) The average bonded ball roundness has a value of at most 0.0025 μm ,
provided the wire has an average diameter of 18 μm ;
30 η) The average bonded ball concentricity has a value of at most 0.00056 μm ,
provided the wire has an average diameter of 18 μm .

11. A process for the manufacture of a wire of any one of the preceding claims, the process comprising at least the process steps of

(1) providing a precursor item comprising or consisting of:

(a) nickel in an amount in the range of from 0.005 to 5 wt.-%,

(b) optionally, silver in an amount in the range of from 0.005 to 1 wt.-%,

(c) copper in an amount in the range of from 94 to 99.98 wt.-%, and

(d) 0 to 100 wt.-ppm of further components,

wherein all amounts in wt.-% and wt.-ppm are based on the total weight of the precursor item,

(2) elongating the precursor item to form a wire precursor, until the desired diameter of the wire core is obtained; and

(3) annealing the elongated wire precursor obtained after completion of process step (2).

12. The process of claim 11,

wherein

the annealing is strand annealing.

13. The process of claim 11 or 12,

wherein

the annealing is performed at an object temperature in the range of 440 to 700 °C for 0.1 to 0.4 seconds.

14. The process of claim 11, 12 or 13,

wherein

the annealing is performed at a temperature above the temperature of maximum elongation wherein the elongation value of the wire after annealing is not more than 98% of the maximum elongation value.

15. The process of any one of claims 11 to 14,

wherein

the annealing is performed in an inert or reducing atmosphere.