

Secondary Alloyed 1N Copper Wire for Bonding in Microelectronics Device

FIELD OF INVENTION

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The present invention relates broadly to a secondary alloyed 1N copper wire for bonding in microelectronics

BACKGROUND

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Fine Au, Cu and Al wires are widely used for interconnections in integrated chips. Silver wires have also been examined for unique applications. For Au and Al wires, usually 2N to 4N purity (99 to 99.99%) are applied, while for Cu typically only 4N purity is used. 5N to 8N purity Cu have been examined but are not in practice. Dopants are added for specific applications such as loop capabilities, reliability, bondability, corrosion resistance, etc. Wires in the range of typically 18 μ m to 75 μ m diameter are commonly used in wire bonding. For high current carrying applications, wires in the diameter range of typically 200 μ m to 400 μ m are applied.

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The alloys for the wire are typically continuous cast into rods of diameter of 2mm to 25mm and are further drawn in steps of what is referred to as heavy, intermediate and fine. The fine drawn wires were annealed at high temperature around 0.25 to 0.6 T_m (melting point of the wire) and later spooled, vacuum packed and stored for bonding.

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Several patents reported the benefit of doped and alloyed Cu wire. Pd addition in the range of 0.13 to 1.17mass% claims to have high reliability on pressure cooker test (PCT) test. Cu wire doped with Mg and P <700ppm, maintaining 30ppm of oxygen (O) and with a list of addition of elements Be, Al, Si, In, Ge, Ti, V (6-300ppm), Ca, Y, La, Ce, Pr, Nd <300ppm was found to be good for bonding. Addition of Nb and P in the range of 20-100ppm along with the elements Cs, Lu, Ta, Re, Os, Ir, Po, At, Pr, Pm, Sm, Gd <50ppm and Zr, Sn, Be, Nd, Sc, Ga, Fr, Ra <100ppm revealed soft and bondable wire. A bondable Cu wire was produced when doped with a maximum of 1000ppm of the elements Mn, Co, Ni, Nb, Pd, Zr and In. If the wire contained Be, Fe, Zn, Zr, Ag, Sn, V

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<2000ppm, it was found to be bondable and reliable. Addition of boron (B) up to 100ppm and a small amount of addition of Be, Ca, Ge <10ppm, and at the same time maintaining sulfur (S) <0.5ppm exhibited low ball hardness and reduced work hardening. Cu wire with Cr <25ppm, Zr<9ppm, Ag<9ppm, Sn<9ppm demonstrated good bondability as good as Au wire. Low level addition of Fe, Ag, Sn, Zr <9ppm produced a normal bondable wire. Addition of the elements of B, Na, Mg, Al, Si, Ca, K, V, Ga, Ge, Rb, Sr, Y, Mo, Cd, Cs, Ba, Hf, Ta, Ti, W <1000ppm revealed superior properties and suitable for bonding.

Cu wire processed using ultra high purity Cu such as 8N (99.999999%) having O, C, H, N, S, P <1ppm produced soft wire with 40HV hardness. Cu wires processed using purity 5N and 6N and doped with any one of the elements or combined with different combinations of Ti, Cr, Fe, Mn, Ni, Co and maintaining <4.5ppm showed good bondability. Combination of the addition of Hf, V, Ta, Pd, Pt, Au, Cd, B, Al, In, Si, Ge, Pb, S, Sb, and Bi <4.5ppm with Nb < 4.5ppm using 5N and 6N purity also showed good bondability. Addition of Ti of 0.12-8.4ppm along with Mg, Ca, La, Hf, V, Ta, Pd, Pt, Au, Cd, B, Al, In, Si, Ge, Pb, P, Sb, Bi, Nb of <0.16-8.1ppm were suitable for bonding. A Cu wire with an impurity of <4ppm and containing Mg, Ca, Be, In, Ge, Ti <1ppm performed equal to Au wire and as soft as 35HV.

A clean spherical free air ball was achieved using 4N Cu wire containing Mg, Al, Si, P <40ppm. Similarly, a Cu wire of 40 to 50HV was attained, maintaining a purity < 10ppm with addition of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, Y <20ppm or Mg, Ca, Be, Ge, Si <20ppm. Cu wire with an addition of Ni and Co <100ppm and Ti, Cr, Mn, Fe, Ni, Zr, Nb, Pd, Ag, In, Sn <150ppm showed corrosion resistant and hardness of 41HV. Also Cu wire containing Ti, Fe, Cr, Mn, Ni, Co <150ppm performed quite well on bonding. A soft Cu wire with <49HV was attained using zone refined Cu and maintaining Mg, Ca, Ti, Zr, Hf <100ppm. Addition of elements Be, Sn, Zn, Zr, Ag, Cr, Fe to a maximum 2wt% maintained H, N, O, C contents and control gas creation (H₂, CO, N₂, O₂) during free air ball, consequently attained a superior bond strength. Adding 400ppm of Mg, traces of Fe and Ag showed reduction in crack formation near the heat affected zone (HAZ). The wire was corrosion resistant and it was processed using 6N

purity Cu. Addition of La<0.002wt%, Ce<0.003wt%, Ca<0.004wt% to a 4N Cu wire revealed a long storage life.

Generally, secondary alloyed Cu wires are in demand with good bondability, free air ball formation in an inert or reactive environment, reliability, in particular under highly accelerated stress test (HAST), good looping performance and easy to wire draw in mass production scale properties. Slight increase in the resistivity by 5-15% is typically the disadvantage of doped Cu wires. However, if the wire exhibits superior reliability performance especially under HAST, the wire is attractive even with increased resistivity and cost.

Example embodiments of the present invention seek to provide 1N secondary alloyed Cu wire for bonding in microelectronics that can provide high reliability performance with reduced compromises in other properties.

SUMMARY

According to an aspect of the present invention, there is provided a secondary alloyed 1N copper wire for bonding in microelectronics comprising at least one of Pd, Au, and Pt as corrosion resistance alloying material, wherein a concentration of said corrosion resistance alloying material is between 0.99wt% and 9.9wt%.

The corrosion resistance alloying material may comprise 1.18wt% to 9.9wt% of Pd.

The corrosion resistance alloying material may comprise 0.99wt% to 9.9wt% of Au.

5 The corrosion resistance alloying material may comprise 0.99wt% to 9.9wt% of Pt.

The corrosion resistance alloying material may comprise 0.005wt% to 0.1wt% of Ag and 0.09wt% to 9.8wt% of Pd.

10 The corrosion resistance alloying material may comprise 0.005wt% to 0.1wt% of Ag and 0.09wt% to 9.8wt% of Au.

The corrosion resistance alloying material may comprise 0.005wt% to 0.1wt% of Ag and 0.09wt% to 9.8wt% of Pt.

15 The corrosion resistance alloying material may comprise about 0.005wt% to about 0.1wt% of Ag and about 0.09wt% to about 9.6wt% of Ni.

20 The corrosion resistance alloying material may comprise about 0.005wt% to about 0.1wt% of Ag and about 0.09wt% to about 9.6wt% of Pd.

The corrosion resistance alloying material may further comprise about 0.008wt% of P.

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The corrosion resistance alloying material may further comprise about 0.005wt% to 0.013wt% of a deoxidizer alloying material.

5 The deoxidizer alloying material may comprise about 0.005wt% of Ca, Ce, Mg, La and Al.

The deoxidizer alloying material may further comprise about 0.008wt% of P.

10 The corrosion resistance alloying material may comprise 0.005wt% to 0.1wt% of Ag, 0.09wt% to 9.6wt% of Ni, 0.005wt% of Ca, Ce, Mg, La and Al, and 0.008wt% of P.

The corrosion resistance alloying material may comprise 0.005wt% to 0.1wt% of Ag, 0.09wt% to 9.6wt% of Pd, 0.005wt% of Ca, Ce, Mg, La and Al, and 0.008wt% of P.

15 The corrosion resistance alloying material may further comprise 0.02wt% to 0.29wt% of a grain refiner alloying material.

20 The grain refiner alloying material may comprise 0.005wt% to 0.2wt% of Fe, 0.005wt% to 0.05wt% of B, 0.005wt% to 0.02wt% of Zr, and 0.005wt% to 0.02wt% of Ti.

The secondary alloyed 1N copper wire may further comprise 0.0003wt% of S.

BRIEF DESCRIPTION OF THE DRAWINGS

5 Embodiments of the invention will be better understood and readily apparent to one of ordinary skill in the art from the following written description, by way of example only, and in conjunction with the drawings, in which:

10 Fig. 1 shows comparative tensile stress-strain data illustrating for secondary alloyed 1N Cu wires according to an example embodiment.

 Fig. 2 shows comparative polarization scan data for secondary alloyed 1N Cu wires according to an example embodiment.

15 Figs. 3a) - c) show SEM images illustrating loop, ball, and stitch bonds respectively for secondary alloyed 1N Cu wires according to an example embodiment.

20 Figs. 4a) - b) show comparative ball bond and stitch bond process window data respectively for secondary alloyed 1N Cu wires according to an example embodiment.

25 Figs. 5a) - b) show comparative thermal ageing (also referred to as high temperature storage (HTS)) data for secondary alloyed 1N Cu wires according to an example embodiment.

 Figs. 6a) - c) show comparative loop height data, and SEM images of low loop bands respectively for secondary alloyed 1N Cu wires according to an example embodiment.

DETAILED DESCRIPTION

5 The example embodiments described herein can provide 1N secondary alloyed Cu wire for bonding in microelectronics packaging industries. The major secondary alloying elements are Ag, Ni, Pd, Au, Pt, Cr, Ca, Ce, Mg, La, Al, P, Fe, B, Zr and Ti, using high purity Cu (>99.99%). Fine wires are drawn from the alloyed Cu. The wires in
10 example embodiments are bondable to Al bond pads as well as Ag, Cu, Au, Pd plated surfaces. The results of HTS of the wire bonds are comparable to a commercially available 4N soft Cu reference wire, when bonded to an Al bond pad and stored at about 175°C for about 1000 hours. Corrosion resistance of the secondary alloyed wires is advantageously better than the 4N soft Cu reference wire. As will be appreciated by a person skilled in the art, HAST or THB (temperature humidity bias) tests are typically
15 conducted for Cu wire bonded and epoxy molded devices, and for bias or unbiased conditions. During the test, the Cu wire bond interface (i.e. Cu wire welded to Al bond pad) undergoes electro-chemical based galvanic corrosion. Moisture absorption by the epoxy is the source for diffusion of hydroxyl ions (OH^-). Parts per million level of halogen (Cl, Br, etc.) contamination in the epoxy is the source for Cl^- ions. Polarisation scans
20 recorded for wires according to example embodiments of the present invention under an electrochemical reaction of the wire in dilute HCl acid, revealed a positive rest potential exhibiting corrosion resistance. Hence, 1N secondary alloyed Cu wires according to example embodiments are expected to perform better on reliability studies such as HAST and THB.

25 The secondary alloyed 1N Cu is continuous cast into rods. Elements are added individually or combined to a maximum of about 9.9 wt% and maintaining the composition of the wire to be 1N in the example embodiments. The cast rods are wire drawn to a fine diameter of about 10 μm to 250 μm . The fine wires in example
30 embodiments advantageously exhibit good free air ball (FAB) formation, bondability, loop formation and reliability (HTS). Surface oxidation and fusing current of the secondary alloyed wires in example embodiments are close to the 4N soft Cu reference wire, for bonding in microelectronics packaging sectors. Hardness, tensile strength and

electrical resistivity of the secondary alloyed Cu wires according to example embodiments are slightly higher than for the 4N soft Cu reference wire. The secondary alloyed 1N wires according to example embodiments advantageously reveal better corrosion resistance without compromising softness drastically.

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In the example embodiments, copper of 4N to 5N purity was used to prepare the alloys and was melted in a vacuum induction furnace. At least one or more of Ag, Ni, Pd, Au, Pt, Cr, Ca, Ce, Mg, La, Al, P, Fe, B, Zr and Ti were added into the melt and held for about 2 to 15 minutes to allow a thorough dissolution. The elements were added
10 individually or combined. The alloy was continuous cast into about 2mm to 25mm rods at a slow speed. No significant loss in dopant additions was observed. These rods were cold wire drawn at room temperature (about 23-25°C).

A tungsten carbide die was used to initially draw heavy wire, and a diamond die
15 was used for further reduction to fine wire. The wire was drawn in three stages at a drawing speed of about 15m/s and less. The die reduction ratios were about 14-18% for heavy wires and about 4 to 12% for fine wires. During cold drawing, the wires were lubricated and intermediate annealed between stages to reduce the residual stresses. Finally, the drawn wires were strand annealed, spooled on clean anodized (plated)
20 aluminum spools, vacuum packed and stored.

Hardness was measured using a Fischer scope H100C tester with a Vickers indenter applying 15mN force for 10s dwell time. Tensile properties of the wires were tested using Instron-5300. The wires were bonded using a Kulicke & Soffa (K&S) - iConn
25 bonder. The bonded wires were observed in a LEO-1450VP scanning electron microscope.

The elements secondary alloyed and ranges of additions in the example embodiments are provided in Table 1. Nobel metals Ag, Au, Pd, Pt, and metals Ni and
30 Cr are alloyed to improve the corrosion resistance of the Cu wire. Ca, Ce, Mg, La, Al, P are alloyed in some embodiments as a deoxidizer, softening the FAB. Fe, B, Zr, Ti are alloyed in some embodiments as a grain refiner to influence FAB grains. Boron is added in some embodiments to influence the strain hardening of the wire along with Ag and Ni.

Table 1 - Composition (wt%) of 1N secondary alloyed Cu wire

Alloy/ Element	Ag	Ni	Pd	Au	Pt	Cr	Ca+ Ce	Mg + La	Al	P	S	Fe	B	Zr	Ti	Total
4N soft Cu	<0.01 2	each <0.0002									each <0.0003	each <0.0002				<100 wt.ppm
1	0.99- 9.9	-	-	-	-	-	-	-	-	-	0.0003	-	-	-	-	≤9.95
2	-	0.99 -9.9	-	-	-	-	-	-	-	-		-	-	-	-	≤9.95
3	-	-	1.18 -9.9	-	-	-	-	-	-	-		-	-	-	-	≤9.95
4	-	-	-	0.99 -9.9	-	-	-	-	-	-		-	-	-	-	≤9.95
5	-	-	-	-	0.99 -9.9	-	-	-	-	-		-	-	-	-	≤9.95
6	-	-	-	-	-	0.99 -9.9	-	-	-	-		-	-	-	-	≤9.95
7	0.005 -0.1	0.09 -9.8	-	-	-	-	-	-	-	-		-	-	-	-	≤9.95
8	0.005 -0.1	-	0.09 -9.8	-	-	-	-	-	-	-		-	-	-	-	≤9.95
9	0.005 -0.1	-	-	0.09 -9.8	-	-	-	-	-	-		-	-	-	-	≤9.95
10	0.005 -0.1	-	-	-	0.09 -9.8	-	-	-	-	-		-	-	-	-	≤9.95
11	0.005 -0.1	-	-	-	-	0.09 -9.8	-	-	-	-		-	-	-	-	≤9.95
12	0.005 -0.1	0.09 -9.8	-	-	-	-	-	-	-	0.008		-	-	-	-	≤9.95
13	0.005 -0.1	-	0.09 -9.8	-	-	-	-	-	-	0.008		-	-	-	-	≤9.95
14	0.005 -0.1	-	-	0.09 -9.8	-	-	-	-	-	0.008		-	-	-	-	≤9.95
15	0.005 -0.1	-	-	-	0.09 -9.8	-	-	-	-	0.008		-	-	-	-	≤9.95
16	0.005 -0.1	-	-	-	-	0.09 -9.8	-	-	-	0.008		-	-	-	-	≤9.95
17	0.005 -0.1	0.09 -9.8	-	-	-	-	0.005			-		-	-	-	-	≤9.95
18	0.005 -0.1	-	0.09 -9.8	-	-	-	0.005			-		-	-	-	-	≤9.95
19	0.005 -0.1	0.09 -9.8	-	-	-	-	0.005			0.008		-	-	-	-	≤9.95
20	0.005 -0.1	-	0.09 -9.8	-	-	-	0.005			0.008		-	-	-	-	≤9.95
21	0.005 -0.1	0.09 -9.6	-	-	-	-	0.005			0.008		0.00 5- 0.2	0.00 5- 0.05	0.00 5- 0.02	0.00 5- 0.02	≤9.95
22	0.005 -0.1	-	0.09 -9.6	-	-	-	0.005			0.008		0.00 5- 0.2	0.00 5- 0.05	0.00 5- 0.02	0.00 5- 0.02	≤9.95

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The mechanical and electrical properties of the secondary alloyed wires of the example embodiments are provided in Table 2. The properties advantageously are close to the 4N soft Cu reference wire. A representative tensile plot of 1N secondary alloyed Cu wire according to example embodiments is shown in Figure 1. As can be seen from a

comparison of curve 100 (1N secondary alloyed Cu wire according to example embodiments) and curve 102 (the 4N soft Cu reference wire), the deformation behavior is advantageously similar on tensile loading, but may require higher load to plastically deform. The hardness and modulus of 1N secondary alloyed Cu wire according to example embodiments are higher. The electrical resistivity of the 1N secondary alloyed Cu wire according to example embodiments is higher than that of 4N Au wires of about 2.34 $\mu\Omega$.cm. This demonstrates that a maximum of about 9.9 wt% secondary alloying does not alter the deformation characteristics, modulus, hardness and electrical resistivity of the secondary alloyed wire additions in example embodiments drastically.

Table 2 - Corrosion, mechanical and electrical properties of 1N secondary alloyed Cu wires

Alloy/ Element	Wire Hardness (15mN/10s), HV	FAB Hardness (15mN/10s), HV	Modulus, GPa	Resistivity, $\mu\Omega$.cm	Fusing current (for 10mm length, 300ms input pulse time), mA	Corrosion resistant (++++Excellent, +++very good, ++Good, +Satisfactory)
4N soft Cu	~85	~85	~90	~1.7	~340	
1	~95	~95	~97	~3.3	~340	+
2	~95	~95	~97	~3.3	~340	++
3	~95	~95	~97	~3.3	~340	++++
4	~95	~95	~97	~3.3	~340	++
5	~95	~95	~97	~3.3	~340	++++
6	~95	~95	~97	~3.3	~340	++
7	~95	~95	~97	~3.3	~340	++
8	~95	~95	~97	~3.3	~340	++++
9	~95	~95	~97	~3.3	~340	++
10	~95	~95	~97	~3.3	~340	++++
11	~95	~95	~97	~3.3	~340	++
12	~95	~95	~97	~3.3	~340	++
13	~95	~95	~97	~3.3	~340	++++
14	~95	~95	~97	~3.3	~340	++
15	~95	~95	~97	~3.3	~340	++++
16	~95	~95	~97	~3.3	~340	++
17	~95	~95	~97	~3.3	~340	++
18	~95	~95	~97	~3.3	~340	++++
19	~95	~95	~97	~3.3	~340	++
20	~95	~95	~97	~3.3	~340	++++
21	~95	~95	~97	~3.3	~340	++
22	~95	~95	~97	~3.3	~340	++++

The corrosion resistance of 1N secondary alloyed Cu wires according to example embodiments is much better than that of the 4N soft Cu reference wire (Table 2). Figure 2 shows a representative scan of the 1N secondary alloyed Cu wire according to

example embodiments (curve 200), revealing a higher positive rest potential of -96mV compared to -255mV for the 4N soft Cu reference wire (curve 202). As will be appreciated by a person skilled in the art, in a polarization scan, if the rest potential (corrosion potential) of the test element is towards positive, the element is noble. On the other hand, if the rest potential is negative the element is active (corrosive). Therefore, the 1N secondary alloyed Cu wire according to example embodiments is "nobler" than the 4N soft Cu reference wire. The scan was obtained using dilute HCl acid electrolyte and stirring the solution kept at room temperature.

The 1N secondary alloyed Cu wire of example embodiments can be bonded to pads metallized (plated) with Au, Ag, Pd and Cu. On bonding to Al bond pad, the wire bonds are anticipated to have a longer reliability life especially under HAST and THB tests. Figures 3(a), (b) and (c) show representative scanning electron microscope images of loop, ball and stitch bonds respectively of a 1N secondary alloyed Cu 0.8mil wire according to example embodiments. With reference to Figures 4 and 5, the ball and stitch bond process window and reliability performance of the 1N secondary alloyed Cu wire according to example embodiments and of the reference soft Cu 4N wires are nearly the same. More particular, in Fig. 4(a), the representative ball bond process window 400 for the 1N secondary alloyed Cu wire according to example embodiments is similar to the ball bond process window 402 of the 4N soft Cu reference wire. Similarly, in Fig. 4(b) the representative stitch bond process window 404 for the 1N secondary alloyed Cu wire according to example embodiments is similar to the stitch bond process window 406 for the 4N soft Cu 0.8mil reference wire. A comparison of curve 500 (Fig. 5(a)) and representative curve 502 (Fig. 5(b)) illustrates that the thermal aging of the 4N soft Cu 0.8mil reference wire and the 1N secondary alloyed Cu 0.8mil wire according to example embodiments are also similar.

Ultra low loop bonding of 1N secondary alloyed Cu wire according to example embodiments for 2.4mil height also revealed good capability similar to the 4N soft Cu reference wire. More particular, the plot in Fig. 6(a) shows the representative loop height measured for the bonded 1N secondary alloyed Cu 0.8mil wire according to example embodiments (at numeral 600) is substantially the same as for the 4N soft Cu 0.8mil reference wire (at numeral 602). This indicates that 1N secondary alloyed Cu wires

according to example embodiments are soft and perform as good as the 4N soft Cu reference wire. Scanning electron microscope (SEM) images of 1N secondary alloyed Cu 0.8mil wires (Figs 6(b), (c)) showed no obvious crack in the neck region for the wires according to example embodiments.

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It will be appreciated by a person skilled in the art that numerous variations and/or modifications may be made to the present invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects to

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be illustrative and not restrictive.

CLAIMS

1. A secondary alloyed 1N copper wire for bonding in microelectronics comprising at least one of Pd, Au, and Pt as corrosion resistance alloying material, wherein a concentration of said corrosion resistance alloying material is between 0.99wt% and 9.9wt%.

2. The secondary alloyed 1N copper wire as claimed in claim 1, wherein the corrosion resistance alloying material comprises 1.18wt% to 9.9wt% of Pd.

3. The secondary alloyed 1N copper wire as claimed in claim 1, wherein the corrosion resistance alloying material comprises 0.99wt% to 9.9wt% of Au.

4. The secondary alloyed 1N copper wire as claimed in claim 1, wherein the corrosion resistance alloying material comprises 0.99wt% to 9.9wt% of Pt.

5. The secondary alloyed 1N copper wire as claimed in claim 1, wherein the corrosion resistance alloying material comprises 0.005wt% to 0.1wt% of Ag and 0.09wt% to 9.8wt% of Pd.

6. The secondary alloyed 1N copper wire as claimed in claim 1, wherein the corrosion resistance alloying material comprises 0.005wt% to 0.1wt% of Ag and 0.09wt% to 9.8wt% of Au.

5 7. The secondary alloyed 1N copper wire as claimed in claim 1, wherein the corrosion resistance alloying material comprises 0.005wt% to 0.1wt% of Ag and 0.09wt% to 9.8wt% of Pt.

8. The secondary alloyed 1N copper wire as claimed in any one of claims 5
10 to 7, further comprising 0.008wt% of P.

9. The secondary alloyed 1N copper wire as claimed in claim 5, further comprising 0.005wt% to 0.013wt% of a deoxidizer alloying material.

15 10. The secondary alloyed 1N copper wire as claimed in claim 9, wherein the deoxidizer alloying material comprises 0.005wt% of Ca, Ce, Mg, La and Al.

11. The secondary alloyed 1N copper wire as claimed in claim 10, wherein the deoxidizer alloying material further comprises 0.008wt% of P.

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12. The secondary alloyed 1N copper wire as claimed in claim 1, wherein the corrosion resistance alloying material comprises 0.005wt% to 0.1wt% of Ag and 0.09wt% to 9.8wt% of Pd, and wherein the secondary alloyed 1N copper wire further comprises 0.005wt% of Ca, Ce, Mg, La and Al, and 0.008wt% of P.

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13. The secondary alloyed 1N copper wire as claimed in claim 1, wherein the corrosion resistance alloying material comprises 0.005wt% to 0.1wt% of Ag and 0.09wt% to 9.6wt% of Pd, and wherein the secondary alloyed 1N copper wire further comprises 0.005wt% of Ca, Ce, Mg, La and Al, and 0.008wt% of P.

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14. The secondary alloyed 1N copper wire as claimed in claim 12 or 13, further comprising 0.02wt% to 0.29wt% of a grain refiner alloying material.

15. The secondary alloyed 1N copper wire as claimed in claim 14, wherein the grain refiner alloying material comprises 0.005wt% to 0.2wt% of Fe, 0.005wt% to 0.05wt% of B, 0.005wt% to 0.02wt% of Zr, and 0.005wt% to 0.02wt% of Ti.

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16. The secondary alloyed 1N copper wire as claimed in any one of the preceding claims, further comprising 0.0003wt% of S.

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