

EXTRA FINE COPPER WIRE AND PROCESS FOR PRODUCING THE SAME

FIELD OF THE INVENTION

The invention relates to an extra fine copper wire and a
5 process for producing the same. More particularly, the invention
relates to an extra fine copper wire which is suitable particularly
as a core wire of an extra fine enamel wire and a process for producing
the same.

10 BACKGROUND OF THE INVENTION

Extra fine enamel wires with a diameter of 0.02 to 0.05 mm
have been used for coils and the like in stepping motors of watches,
magnetic heads for magnetic recording, fly-back transformers for
cathode-ray tubes and the like. High purity coppers having an oxygen
15 content of not more than 0.1% (hereinafter referred to as "pure
copper"), such as tough pitch copper and oxygen free copper, have
been used in core wires of the extra fine enameled wires.

Pure copper advantageously has high electrical conductivity
and high thermal conductivity, and has also been used not only as
20 core wires of extra fine enameled wires, but also as lead wires in
components of electronic equipment.

Pure copper subjected to cold working, however, is
disadvantageously softened at high temperatures as a result of
recrystallization. When pure copper is used as a core wire of an
25 extra fine enamel wire, this is one of major causes of breaking of
wire at the time of wire drawing in the production process. The
softening is caused by heat of friction between the material and
a die. The softened material cannot withstand tension created in

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drawing using the die, resulting in breaking of wire. This type of breaking of wire is likely to occur when the degree of drawing (reduction in area) is 95% or more. Therefore, the smaller the wire diameter, the higher the frequency of breaking of wire.

5 Softening of the copper material due to recrystallization proceeds even at room temperature, and, after wire drawing, poses a problem of a reduction in tensile strength and elongation with the elapse of time. Copper wires which have been subjected to drawing to a final wire diameter causes a lowering in tensile
10 strength and elongation with the elapse of time during storage thereof. This is particularly significant in the case of high purity copper called oxygen free copper (for example, purity of 5 N or 6 N). Even in the case of a tough pitch copper having a purity in the 3 N class, this phenomenon occurs when the degree of wire drawing
15 is high.

The recrystallization at room temperature locally occurs in the material, and inspection of the metallographic structure in the recrystallized portion reveals that particular grains are grown and coarsened. Annealing of this core wire in the production process
20 of enamel wires leads to the formation of new fine grains, which creates a structure wherein newly formed fine grains and already existing coarsened grains are present as a mixture. This appears to be causative of a reduction in tensile strength and elongation, because copper materials, which do not cause softening at room
25 temperature, have such a metallographic structure that grains are fine and homogeneous. The higher the degree of the reduction in area in the step of wire drawing and the higher the storage temperature, the higher the degree of softening of the drawn copper

wires at room temperature.

Reducing the degree of the reduction in area in the step of wire drawing and increasing the number of times of annealing conducted in a period between a first wire diameter and wire drawing to a final wire diameter are considered as effective in reducing the breaking of wire at the time of wire drawing and the softening during storage at room temperature.

According to the conventional extra fine copper wires, however, the breaking of wire cannot be prevented without lowering the degree of wire drawing by increasing the number of times of annealing. This incurs an increase in production cost. As explained above, in the prior art, use of high purity copper having an oxygen content of not more than 0.1%, such as tough pitch copper and oxygen free copper, in copper wires for core wires of extra fine enameled wires have often created breaking of wire in the step of wire drawing, and, after wire drawing, caused a reduction in tensile strength and elongation with the elapse of time during storage at room temperature. The breaking of wire at the time of wire drawing is likely to occur when the degree of wire drawing is high. Also regarding the reduction in tensile strength and elongation during storage of wires after wire drawing, the higher the degree of wire drawing, the larger the reduction in tensile strength and elongation. The latter is particularly significant in the case of high-purity, oxygen-free copper of 5 N or more. In the case of high degree of wire drawing, however, the reduction in tensile strength and elongation has occurred even in a tough pitch copper having a purity in the 3 N class. Reducing the degree of the reduction in area at the time of wire drawing can reduce the breaking of wire at the time of wire

drawing and the softening during storage at room temperature. In this case, however, the number of times of annealing conducted in a period between a first wire diameter and wire drawing to a final wire diameter should be increased, resulting in increased production cost.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the invention to provide an extra fine copper wire at lowered production cost through the prevention of breaking of wires in the course of wire drawing and prevention of an increase in the required number of times of annealing conducted between a first wire diameter and wire drawing to a final wire diameter in the production process of extra fine copper wires of tough pitch copper.

It is another object of the invention to prevent a reduction in tensile strength and elongation with the elapse of time during storage at room temperature after wire drawing of extra fine copper wires of tough pitch copper.

It is a further object of the invention to provide a process for producing an extra fine copper wire of tough pitch copper that can prevent breaking of wire at the time of wire drawing, can avoid an increase in the required number of times of annealing conducted between wire drawings to lower the production cost, and can produce an extra fine copper wire which, after wire drawing, creates no significant lowering in tensile strength and elongation with the elapse of time during storage at room temperature.

According to the first feature of the invention, an extra fine copper wire has a diameter of 0.02 to 0.05 mm and comprises a tough pitch copper having an oxygen content of more than 100 to 500 ppm,

wherein the extra fine copper wire is constituted by an annealed copper wire having a tensile strength of less than a predetermined value and further comprises 5 to less than 200 ppm by weight of at least one metal selected from tin and indium.

5 According to the second feature of the invention, a process for producing an extra fine copper wire, with a diameter of 0.02 to 0.05 mm, comprising a tough pitch copper having an oxygen content of more than 100 to 500 ppm, comprises the step of casting a tough pitch copper, wherein, in the step of casting, at least one metal
10 selected from tin and indium is added in an amount of 5 to less than 200 ppm by weight based on the weight of the extra fine copper wire.

 According to the third feature of the invention, an extra fine enamel wire comprises: an extra fine copper wire as a core wire, with a diameter of 0.02 to 0.05 mm, comprising a tough pitch copper
15 having an oxygen content of more than 100 to 500 ppm, said extra fine copper wire being constituted by an annealed copper wire having a tensile strength of less than a predetermined value and further comprising 5 to less than 200 ppm by weight of at least one metal
 selected from tin and indium; and an enamel coating covering the
20 core wire.

 The extra fine copper wire of tough pitch copper according to the invention or produced according to the process of the invention has a diameter of 0.02 to 0.05 mm and is constituted by an annealed copper wire having a tensile strength of less than 35
25 kg/mm². The tough pitch copper constituting the extra fine copper wire contains 5 to less than 200 ppm by weight of tin or indium or both tin and indium (hereinafter referred to as "additive element"). The tough pitch copper refers to high purity copper containing about

100 to 500 ppm of oxygen. The oxygen content of the tough pitch copper is generally 200 to 400 ppm.

Tin and indium are elements having high affinity for oxygen, and, when added to a tough pitch copper having an oxygen content of not more than 500 ppm, form a solid solution to increase the softening temperature of copper. The amount of the additive element added is 5 to less than 200 ppm by weight. When the amount of the additive element added is less than 5 ppm, the degree of an increase in softening temperature of copper is so small that breaking of wire at the time of wire drawing and a reduction in tensile strength and elongation with the elapse of time during storage at room temperature after wire drawing cannot be satisfactorily prevented. On the other hand, when the amount of the additive element added is not less than 200 ppm, this amount exceeds the upper limit of the amount of the additive element which can form a solid solution in the presence of oxygen. Therefore, the effect of increasing the softening temperature is saturated. Further, addition of the additive element in an amount exceeding the upper limit unfavorably results in the formation of an increased amount of tin oxide.

The additive element is added to tough pitch copper as a base material at the time of casting. In the casting, a boat type ceramic crucible may be used, or alternatively, a continuous casting apparatus, such as SCR, may be used. In the case of continuous casting, the effect attained by the additive element is large because cooling in the step of casting is rapid resulting in forcible formation of solid solution of the additive element.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be explained in more detail in conjunction with the appended drawing, wherein:

Fig. 1 is a graph showing the relationship between the heat treatment temperature and the tensile strength for copper materials.

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DESCRIPTION OF THE PREFERRED EMBODIMENTS

One of preferred embodiments of the invention will be explained in detail.

Tough pitch copper containing 200 to 400 ppm of oxygen was cast using an SCR continuous casting apparatus and then wire rod having a diameter of 8 mm were produced. At the time of casting, tin, indium, or both tin and indium were added to molten copper with varied amounts to cast 12 copper materials for core wires.

For comparison, copper having a high purity of 6 N was cast using a small-size continuous casting machine to prepare a diameter of 8 mm wire rod (prior art). The content of tin and indium in the 13 copper materials was quantitatively determined by ICP. The results are summarized in Table 1. Material Nos. 1 to 5 had chemical compositions falling within the scope of the invention, while material Nos. 6 to 13 were comparative materials having chemical compositions outside the scope of the invention.

Table 1

Classification		Invention					Comparative		
No.		1	2	3	4	5	6	7	8
Content, wt.ppm	Tin	20	75	3	4	100	3	<1	2
	Indium	<1	<1	60	95	50	0	<1	2
	Total	20	75	63	99	150	3	4	4

Classification		Comparative					
No.		9	10	11	12	13	
Content, wt.ppm	Tin	220	3	70	3000	<1	
	Indium	<1	280	170	<1	<1	
	Total	220	283	240	3000	<1	

The oxygen content of the wire rods was measured and found to be in the range of 200 to 400 ppm. The wire rods having a diameter of 8 mm were subjected to cold wire drawing to a diameter of 2.6 mm, once annealed, subjected to cold wire drawing to a diameter of 0.9 mm, annealed, and then subjected to cold wire drawing to a diameter of 0.04 mm. The extra fine wires thus obtained were then stored for up to 50 days, and then annealed to prepare core wires for enamel wires.

10 Copper materials according to the invention (Nos. 1 to 5) and copper material Nos. 9, 10, 11, and 12 (comparative copper materials) did not cause breaking of wire at all in the course of wire drawing. On the other hand, copper material Nos. 6, 7, 8, and 13 (comparative copper materials) having a low additive element content caused
15 breaking of wire due to softening.

EXAMPLES

The effect of the invention will be explained in more detail with reference to the following examples.

20 Example 1

At a stage where the wire rods having a diameter of 8 mm for copper material Nos. 1 to 13 shown in Table 1 had been subject to

cold wire drawing to a diameter of 2.6 mm, the wires were heat treated in a salt bath at a temperature in the range of 120 to 400°C for one hr. For the heat-treated wires, the tensile strength was measured with a tensile tester at a stress rate of 20 mm/min.

- 5 Fig. 1 is a diagram showing the relationship between the heat treatment temperature (°C) and the tensile strength (kg/mm²) for the copper material Nos. 2 and 6. In Fig. 1, $\sigma_s(20^\circ\text{C})$ represents the tensile strength of the as-wire-drawn copper materials (temperature 20°C), $\sigma_s(400^\circ\text{C})$ represents the tensile strength of fully annealed materials (heat treatment temperature 400°C). Regarding the half-softening temperature defined as such a heat treatment temperature that the tensile strength is a value ($[\sigma_s(20^\circ\text{C}) + \sigma_s(400^\circ\text{C})]/2$) which is just intermediate between as-wire-drawn material ($\sigma_s(20^\circ\text{C})$) and the fully annealed material ($\sigma_s(400^\circ\text{C})$),
- 10 the copper material No. 2 according to the invention is 20°C above the conventional copper material No. 6. The results of evaluation of wire materials in terms of the above half-softening temperature are summarized in Table 2.

Table 2

Classification		Invention					Comparative		
No.		1	2	3	4	5	6	7	8
Content, wt.ppm	Tin	20	75	3	4	100	3	<1	2
	Indium	<1	<1	60	95	50	<1	4	2
Half-softening temp. °C		190	198	196	200	200	180	180	180
Classification		Comparative							
No.		9	10	11	12	13			

Content,	Tin	220	3	70	3000	<1	
wt.ppm	Indium	<1	280	170	<1	<1	
Half-softening temp.°C		200	200	200	350	133	

For all the copper material Nos. 1 to 5 according to the invention, the half-softening temperature was 10 to 20°C above that of the conventional copper material No. 6. For the copper material Nos. 7 and 8 having low additive element content, the half-softening temperature was the same as that of the conventional copper material No. 6. For the copper material Nos. 9, 10, and 11 having an additive element content exceeding 200 ppm, the half-softening temperature was not above that of the copper material Nos. 4 and 5 (200°C). The copper material No. 12 having an extremely high tin content had a remarkably increased half-softening temperature. The increased half-softening temperature, when the copper material is used as an annealed copper core wire for enamel wires and the like, renders the annealing difficult. On the other hand, the half-softening temperature of the high purity copper No. 13 was low and 133°C.

For the heat-treated, cold drawn wires, the electrical conductivity was measured. The results are summarized in Table 3.

Table 3 :

Classification		Invention					Comparative		
No.		1	2	3	4	5	6	7	8
Content,	Tin	20	75	3	4	100	3	<1	2
wt.ppm	Indium	<1	<1	60	95	50	<1	4	2

Conductivity,								
%IACS		98	98	98	98	97	98	98
Classification		Comparative						
No.		9	10	11	12	13		
Content,	Tin	220	3	70	3000	<1		
wt.ppm	Indium	<1	280	170	<1	<1		
Conductivity,								
%IACS		97	98	97	85	100		

As is apparent from Table 3, among the copper material Nos. 1 to 11, there is substantially no difference in electrical conductivity. The copper material No. 12 having a high tin content had remarkably lowered electrical conductivity. As described above, the copper material No. 12 had a remarkably increased softening temperature. The reason for this is that oxygen contained in the molten copper was entirely reacted with tin to form tin oxide and tin not converted to the tin oxide was dissolved as a solid solution in copper. Further, the formation of the solid solution of tin resulted in remarkably lowered electrical conductivity.

As described in the column of "PREFERRED EMBODIMENTS OF THE INVENTION," after the copper materials was subjected to cold wire drawing to a diameter of 0.04 mm, the materials were then stored at room temperature for 50 days. In this case, before and after the storage, the mechanical properties (tensile strength and elongation) were measured. These materials were further annealed, followed by preparation of enamel wires (1UEW0.04). For the enamel wires, the mechanical properties were measured. For the copper

material Nos. 2, 3, and 5 according to the invention and the comparative copper material Nos. 6, 7, and 13, the results of the measurement of the mechanical properties before annealing are summarized in Table 4, and the results of the measurement of the mechanical properties after annealing are summarized in Table 5.

Table 4: Results before annealing

Classification		Invention			Comparative		
Copper material		No.2	No.3	No.5	No.6	No.7	No.13
Load at break, g	Immediate after production	80.3	79.2	80.1	78.2	78.3	70.4
	After storage for 50 days	77.5	76.9	77.5	65.2	63.3	40.5
Elongation, %	Immediate after production	2.5	2.6	2.4	2.5	2.4	2.4
	After storage for 50 days	2.4	2.5	2.3	1.0	0.9	0.7

Table 5: Results after annealing (enameled wires)

Classification		Invention			Comparative		
Copper material		No.2	No.3	No.5	No.6	No.7	No.13
Load at break, g	Immediate after production	39.0	38.2	39.0	38.5	38.2	35.3
	After storage for 50 days	38.5	38.2	39.0	35.1	35.0	30.0
Elongation, %	Immediate after production	25.0	24.2	25.3	23.2	22.1	22.3
	After storage for 50 days	24.3	24.2	25.2	15.1	16.0	10.3

As is apparent from Table 4, for the copper material Nos. 2, 3, and 5 according to the invention which had been subjected to cold wire drawing, the tensile strength and the elongation were hardly lowered after storage for 50 days. On the other hand, for the comparative copper material Nos. 6, 7, and 13, the tensile strength and the elongation were significantly lowered after storage for 50 days.

As is apparent from Table 5, for the copper material Nos. 2, 3, and 5 according to the invention, annealing of the extra fine wires after storage for 50 days caused only a slight lowering in tensile strength and elongation attributable to the storage. On

the other hand, for the comparative copper material Nos. 6, 7, and 13, annealing of the extra fine wires after storage for 50 days caused a significant lowering in tensile strength and elongation after annealing as compared with the tensile strength and the elongation of the materials which had been annealed immediately after the wire drawing.

For the copper material Nos. 2, 3, and 5 according to the invention, the metallographic structure comprised fine grains after cold wire drawing, after storage for 50 days, and after annealing of the extra fine wire. On the other hand, for the comparative copper material Nos. 6, 7, and 13, the metallographic structure comprised a mixture of coarse grains with fine grains.

Example 2

Copper wires according to the invention or produced according to the process of the invention may be used also as hard copper wires. For example, the copper wires may be brought to solid wires or stranded wires followed by covering with an insulator to prepare cables. In this case, the insulator is extruded onto the core wires at a temperature of 100 to 300°C. Therefore, the core wires are instantaneously heated to high temperatures. For this reason, the core wires were evaluated for the softening in the step of extrusion of the insulator in the production of aerial distribution lines. The results of the measurement of the mechanical properties (tensile strength and elongation) before and after covering of conductors (7/φ 2.0) for aerial distribution lines with an insulator are summarized in Table 6.

Table 6

Classification		Invention			Comparative		
Copper material		No. 21	No. 22	No. 23	No. 24	No. 25	No. 26
Content of additive element, mass ppm	Tin	65	4	20	3	2	2
	Indium	<1	80	30	<1	2	1
Tensile strength, kg/mm ²	Before covering	46.3	45.7	47.0	45.8	45.9	46.0
	After covering	46.0	46.0	46.8	41.1	41.5	41.0

As is apparent from Table 6, upon exposure to heat in the step of extrusion of the insulator, the copper materials (Nos. 24, 25, and 26) outside the scope of the invention was softened and caused a lowering in tensile strength, whereas the copper materials (Nos. 21, 22, and 23) according to the invention were not softened. Thus, the process for producing copper wires according to the invention are also applicable to the process for producing hard copper wires covered with an insulator.

As described above, the extra fine copper wire according to the invention has a diameter of 0.02 to 0.05 mm and comprises a tough pitch copper having an oxygen content of more than 100 to 500 ppm, wherein the extra fine copper wire further comprises 5 to less than 200 ppm by weight of at least one metal selected from tin and indium. By virtue of this constitution, coarse grains do not occur in the

metallographic structure in the course of cold wire drawing, storage after wire drawing, and annealing of the extra fine wire. Therefore, cold wire drawing causes no softening-derived breaking of wire. This eliminates the need to increase the number of times of annealing in the course of cold wire drawing for the purpose of preventing the breaking of wire and hence can in turn prevent an increase in production cost. Further, the extra fine copper wire according to the invention is free from a deterioration in mechanical properties, such as tensile strength and elongation, of core wires attributable to storage after wire drawing or annealing of the extra fine wire.

The process for producing an extra fine copper wire, with a diameter of 0.02 to 0.05 mm, comprising a tough pitch copper having an oxygen content of more than 100 to 500 ppm according to the invention comprises the step of casting a tough pitch copper, wherein, in the step of casting the tough pitch copper, at least one metal selected from tin and indium is added in an amount of 5 to less than 200 ppm by weight based on the weight of the extra fine copper wire. By virtue of this constitution, coarse grains do not occur in the metallographic structure in the course of cold wire drawing, storage after wire drawing, and annealing of the extra fine wire. Therefore, cold wire drawing causes no softening-derived breaking of wire. This eliminates the need to increase the number of times of annealing in the course of cold wire drawing for purposes of preventing the breaking of wire and hence can in turn prevent an increase in production cost. Further, the extra fine copper wire according to the invention is free from a deterioration in mechanical properties, such as tensile strength and elongation, attributable to storage after wire drawing or annealing of the extra fine wire.

The invention has been described in detail with particular reference to preferred embodiments, but it will be understood that variations and modifications can be effected within the scope of the invention as set forth in the appended claims.

WHAT IS CLAIMED IS:



1. An extra fine copper wire, with a diameter of 0.02 to 0.05 mm, comprising a tough pitch copper having an oxygen content of more than 100 to 500 ppm, wherein said extra fine copper wire is constituted by an annealed copper wire having a tensile strength of less than a predetermined value and further comprises 5 to less than 200 ppm by weight of at least one metal selected from tin and indium.
2. The extra fine copper wire according to claim 1, wherein the predetermined value is 35 kg/mm².
3. A process for producing an extra fine copper wire, with a diameter of 0.02 to 0.05 mm, comprising a tough pitch copper having an oxygen content of more than 100 to 500 ppm, said process comprising the step of casting a tough pitch copper, wherein, in the step of casting, at least one metal selected from tin and indium is added in an amount of 5 to less than 200 ppm by weight based on the weight of the extra fine copper wire.
4. The process according to claim 3, wherein the step of casting is carried out using a continuous casting apparatus, such as SCR.
5. An extra fine enameled wire comprising: an extra fine copper wire as a core wire, with a diameter of 0.02 to 0.05 mm, comprising a tough pitch copper having an oxygen content of more than 100 to 500 ppm, said extra fine copper wire being constituted by an annealed copper wire having a tensile strength of less than a predetermined value and further comprising 5 to less than 200 ppm by weight of at least one metal selected from tin and indium; and an enamel coating



covering the core wire.

6. The extra fine enameled wire according to claim 5, wherein the predetermined value is 35 kg/mm².