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(54) Processing copper-magnesium alloys and improved copper alloy wire

(57) In accordance with the present invention, a copper alloy wire having high strength and high conductivity is provided. The copper alloy wire is formed from a copper base alloy containing from 0.05 to 0.9 wt% magnesium and more than 15 ppm impurities in total. The wire has a single end diameter no greater than 0.10 inches, a tensile strength of at least 100 ksi, and an electrical conductivity greater than 60% IACS. A process for producing the copper wire of the present invention is also described.

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Description

BACKGROUND OF THE INVENTION

[0001] The present invention relates to high strength, high conductivity copper alloy wire and a method for manufacturing same, wherein the copper alloy wire is a copper-magnesium based system optionally with one or more additional elements.

[0002] Copper is the natural choice for conductor wire due to its high electrical conductivity. High performance copper alloys are required where the mechanical properties of copper are not sufficient for a particular application. Thus, in addition to electrical conductivity, these copper alloys must also meet a combination of often conflicting properties. These properties may include strength, ductility, softening resistance and flex life. Indeed, ASTM B105 and B624 describe the requirements for hard drawn and high strength, high conductivity copper alloy wire for electrical applications.

[0003] Cadmium copper (alloy C162) is a copper alloy containing 1% nominal cadmium with unique combination of properties. It has an electrical conductivity greater than 80% IACS and when hard can attain a tensile strength in excess of 100 ksi. These properties make the alloy very useful for high strength conductor applications, such as trolley wire or airframe wiring. In addition, this alloy exhibits unusually long flex life as evidenced by the number of cycles it can bend back and forth over a mandrel before fracture. Consequently, it is used in many other high flex conductor applications, such as those in antilock braking harnesses, audio speaker and headset or telephone connecting wire.

[0004] Cadmium has been known to be a health hazard and attempts are being made to replace materials containing this element. Cadmium appears on the list of bio-accumulative and toxic (PBT) chemicals compiled by the Environmental Protection Agency (EPA). The EPA considers cadmium as a possible human carcinogen. Various proposals have been made in different countries to ban or restrict the use of this element. Therefore it is very beneficial to provide alternative alloys to Cu-Cd alloys.

[0005] Cu-Mg alloy base systems offer equally attractive properties. Alloy C18661 with 0.1-0.7 percent Mg is a Cu-Mg alloy listed by Copper Development Association (CDA). Alloy C18665 is another listed alloy with 0.4-0.9% Mg. These alloys may also contain a small amount of residual P which is typically used as a de-oxidant. Although CDA does not list the applications of these alloys, typical applications are as trolley wire or connectors. These alloys are cast and drawn to finish size without any anneal to obtain the highest strength possible.

[0006] It is, therefore, a principal object of the present invention to develop a high strength, high conductivity copper alloy and method for manufacturing same.

[0007] It is a still further object of the present invention to develop an alloy and method as aforesaid, wherein the alloy is a copper base alloy containing magnesium and other elements.

[0008] Further objects of the present invention will appear hereinafter.

SUMMARY OF THE INVENTION

[0009] It has now been found that the foregoing objects can be readily obtained in accordance with the present invention.

[0010] The present invention provides a process for manufacturing a copper alloy wire having a high strength and high conductivity. The process broadly comprises the steps of providing a base material formed from a copper alloy containing from 0.05 to 0.9 wt% magnesium and more than 15 ppm total impurities, cold working the base material into a wire having at least a 40% reduction in original cross section area, performing a restructuring anneal after the cold working step, and drawing the annealed material into a wire having a final gage size of 0.010" maximum. In a preferred method, the magnesium content of the copper alloy is from 0.1 to 0.4 wt%.

[0011] Desirably, the restructuring annealing step is performed at a temperature in the range of 650 to 1050°F for a time period in the range of 1 to 5 hours, preferably 2-3 hours. Desirably, also the copper alloy contains one or more additional alloying ingredients, as from 0.01-0.3 wt% phosphorous,

from 0.01-1.0 wt% iron, preferably less than 0.5 wt% iron,
from 0.01 - 0.5 wt% nickel,
from 0.01 - 0.2 wt% silver,
from 0.01 - 0.2 wt% tin, and preferably less than 0.1 wt% tin, and/or
from 0.01 - 0.5 wt% zinc.

[0012] The present invention also provides an improved copper alloy wire having high strength and high conductivity which broadly comprises a copper alloy containing from 0.05 to 0.9 wt% magnesium and more than 15 ppm impurities, which wire has a single end diameter less than or equal to 0.010 inches, a tensile strength of at least 100 ksi, and an electrical conductivity greater than 60% IACS.

[0013] Further features and advantages of the present invention will appear hereinbelow.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] The present invention will be more readily understandable from a consideration of the accompanying drawings, wherein:

Figure 1 is a graph of tensile strength versus percent reduction in cross sectional area for a copper - 0.12% magnesium alloy processed in accordance with the present and the same alloy processed conventionally;
Figure 2 is a graph similar to Figure 1 for a copper alloy containing 0.15% magnesium and 0.1% tin; and
Figure 3 is a graph of tensile strength versus wire diameter for a copper alloy containing 0.15% magnesium and 0.1% tin processed in accordance with the present invention and the same alloy processed conventionally.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0015] In accordance with the present invention the copper alloy wire contains from 0.05 to 0.9 wt% magnesium, preferably from 0.1 to 0.4 wt%. Increasing the amount of magnesium will increase the strength while reducing the electrical conductivity. This allows the alloy to be tailored to a desired set of properties.

[0016] Additional alloying elements may be added to improve strength or other properties of the alloy. Thus, for example, phosphorous is an element that can be added to increase the strength through precipitation of magnesium phosphide (Mg_3P_2). The amount of phosphorus added to the alloy should not exceed that needed to form the magnesium phosphide, or phosphides of other elements when present. Therefore, the phosphorus should be in an amount less than the amount of magnesium present and generally from 0.01 to 0.3 wt% and preferably from 0.02-0.15 wt%. When phosphorous is added to form phosphide particle, the composition, casting procedure and heat treatment must ensure that the majority of the phosphide particles are sub-micron size to provide high drawability and improved performance at small wire diameters.

[0017] Iron is another beneficial element that may be added to the alloy. For example, copper - magnesium alloys with iron and phosphorus present will form phosphides of magnesium and iron, which are quite beneficial. The amount of iron should vary between 0.01 to 1 wt%, and preferably less than 0.5 wt%.

[0018] Small amounts of tin are also beneficial and serve to slightly improve the strength of the alloy. The amount of tin should desirably vary from 0.01 to 0.2 wt% and preferably less than 0.1 wt%. Very small amounts of tin may be considered as a beneficial impurity. However, larger amounts of tin tend to reduce the electrical conductivity of the alloy.

[0019] Naturally, other alloying additions and conventional impurities greater than 15 ppm in total may be present. For example, small amounts of silver will improve the performance of the alloy without adversely impacting electrical conductivity. Silver, when present, should be in the range of 0.01 to 0.2 wt%. Other alloying additions for effecting specific objectives may include nickel in amount from 0.01 to 0.5 wt% and/or zinc in an amount from 0.01 to 0.5 wt%.

[0020] Thus, the present invention provides non-cadmium containing copper alloy conductors containing magnesium which can readily be used as a replacement for copper-cadmium alloys and in similar applications. The processing of the copper - magnesium alloys to desired final gage wire incorporates at least one restructuring anneal before being drawn to the finish size wire required to manufacture the desired conductor. The resultant wire is characterized by a good combination of strength and conductivity, as well as other desirable properties, such as good flex life and resistance to thermal softening.

[0021] The copper alloy wire of the present invention may be manufactured by the process of providing a base material formed from a copper alloy containing from 0.05 to 0.9 wt% magnesium, cold working the base material into a wire having at least a 40% reduction in original cross section area, performing an anneal, and drawing said material into a wire having a single end final gage of 0.010 inches maximum, preferably the final gage is more than 0.002 inches but less than 0.010 inches. If desired, the copper alloy may also contain one or more of the additional elements discussed above and the annealing step may be performed after the base material has been cold worked into a wire having at least a 70% reduction in the original cross section area.

[0022] The restructuring anneal may be performed at a temperature in the range of 650 to 1050°F for a time period in the range of 1 to 5 hours, preferably at a temperature in the range of 750 to 900°F for a time period in the range of 2 to 3 hours.

[0023] The cold working step may be performed by any suitable technique known in the art including, but not limited to, rolling and/or drawing.

[0024] Copper alloy wires formed in accordance with the present invention exhibit a tensile strength of at least 100 ksi, preferably at least 110 ksi, and an electrical conductivity at room temperature of 68°F greater than 60% IACS, and preferably greater than 70% IACS. This is an unusual set of properties for copper alloy wire products having a single end diameter less than 0.010 inches.

[0025] The foregoing features and others will appear from the following illustrative examples.

EXAMPLE 1

[0026] A copper - magnesium alloy was processed to wire incorporating a restructuring anneal prior to being drawn to finish gage, and for comparison without the anneal. The copper alloy contained 0.12% magnesium. It was surprisingly found that the incorporation of a restructuring anneal in the processing improved the rate of work hardening and provided a stronger wire. Work hardening is the increase in strength of an alloy due to plastic deformation.

[0027] The alloy was cast to 21 mm (0.827 inch) diameter rod and rolled from the 21 mm diameter rod to 7.4 mm (0.291 inch) modified square cross-section. The cross-section is equivalent to 0.312 inch round diameter. The processing of the present invention then provided an anneal at 700-850°F for 1-5 hours, and generally 750-800°F for 2-3 hours, followed by drawing to desired finish gage. The same alloy was drawn to finish gage directly from the 7.4 mm rod using conventional processing which does not employ any annealing.

[0028] The resultant properties are shown in Figure 1 which illustrates the tensile strength of the Cu-Mg alloys processed as aforesaid as a function of cold reduction. It can be readily seen that those alloys given the restructuring anneal obtained an increase of 10 ksi over those not given the anneal. This is a significant increase. It was also found that these alloys could be readily drawn to small diameter wire required for conductor applications, typically less than 0.010 inch diameter.

EXAMPLE 2

[0029] Copper alloys containing 0.15% magnesium and 0.10% tin wire processed in a manner after Example 1, with final gage wire being 38 American Wire Gage (AWG). The alloys were drawn to a final gage either without any anneals (from rod) or after an initial rolling operation followed by a restructuring anneal under the conditions set out in Example 1.

[0030] The resultant properties are shown in Figure 2 which illustrates the tensile strength of the Cu-Mg-Sn alloys processed as aforesaid as a function of percent reduction in area, and in Figure 3 which illustrates tensile strength as a function of wire diameter.

[0031] The results also found that the rate of work hardening of the annealed and drawn wire was greater than that of the wire without any anneal. Work hardening of this alloy as a function of cold reduction in the region of interest is illustrated in Figure 2. At the same cold reduction, an improvement of 20 ksi or greater is observed when the alloy is annealed. When comparing the tensile strength as a function of wire diameter as shown in Figure 3, a similar improvement is found. Depending on the size of the wire, an improvement of 5-10 ksi is obtained when processing of the wire incorporates a restructuring anneal. Figure 3 illustrates that not only can the alloy be drawn to small diameters, but that the obtained tensile strength at 0.004 inch diameter exceeds 120 ksi. The properties of the alloy of the present invention processed in accordance with the present invention are quite attractive and compare favorably with those of copper-cadmium alloy C162.

EXAMPLE 3

[0032] A copper alloy containing 0.15% magnesium was processed in a manner after Example 1. The alloy was given a restructuring anneal following rod rolling. The annealed wire was then drawn to 0.004 inch diameter in several steps. The resultant properties are shown in Table 1, below.

TABLE 1

Diameter, inch	Reduction in Area, %	Tensile Strength, ksi	Electrical Conductivity, % IACS
0.3117	0.0	36.6	86.5
0.2573	31.9	55.0	86.4
0.2159	52.0	63.7	84.1
0.1921	62.0	64.6	83.7
0.1715	69.7	67.5	83.2
0.1583	74.2	65.3	84.6
0.1441	78.6	69.4	83.6

TABLE 1 (continued)

Diameter, inch	Reduction in Area, %	Tensile Strength, ksi	Electrical Conductivity, % IACS
0.1203	85.1	72.2	84.3
0.1010	89.5	74.1	84.3
0.0359	98.7	87.8	84.0
0.0145	99.78	101.9	82.7
0.0040	99.98	121.6	80.8

[0033] Table 1 clearly shows that not only can the alloy be drawn to small diameters, but also that the obtained tensile strength at 0.004 inch diameter exceeds 120 ksi. The properties are quite attractive and compare favorably with those of copper-cadmium alloy C162.

EXAMPLE 4

[0034] One of the major reasons for using high strength conductors is their high flex life. ASTM B470-95 (paragraph 6) describes the test procedures for the flex test. In this test, the conductor is initially hung in a vertical position with a defined weight and is repeatedly flexed back and forth over a pair of standard steel mandrels held in a horizontal position. Flexing of the conductor is repeated until fracture. The number of cycles to fracture defines the flex life.

[0035] In accordance with this example similar conductors were manufactured using alloy C162 (Cu-1% Cd) and a copper alloy containing 0.15% magnesium, with the latter alloy using a restructuring anneal in accordance with the procedure in Example 1. The constructions consisted of 19 ends of 38 AWG wire (0.004 inch diameter). The conductors were flex tested according to the procedure outlined in ASTM B470 outlined above, the results are shown in Table 2, below.

TABLE 2

	Cu-1%Cd	Cu-0.15%Mg
Break Load, 1b	30.9	28.0
Single End Size, inch	0.0041	0.0040
Flex Life	23,617	35,038

In spite of the fact that the copper-cadmium alloy had a higher breaking load (mainly due to a larger size), it showed a lower flex life. Flex life of the copper-magnesium alloy processed in accordance with the present invention is about 50% greater than that of the copper-cadmium alloy. This is quite significant and represents a valuable discovery since flex life represents a major attribute in a high strength conductor.

EXAMPLE 5

[0036] Conductors with 19 ends of 38 AWG construction as in Example 4 were prepared using the copper - 0.15% magnesium - 0.1% tin alloy of Example 2. Two conductors were prepared, one utilizing the no anneal condition and the second utilizing the rod rolled and annealed condition of the wire outlined in Example 1. The conductors were tested for flex life according to ASTM B470 and the results are shown in Table 3, below.

TABLE 3

	Annealed after Initial Rolling	**No Anneal Condition**
Break Load, 1b	29.0	27.3
Single End Size, inch	0.0041	0.0041
Flex Life	34998	28137

As evidenced by a higher break load the above results clearly show a higher strength and a superior flex life for the wire with the restructuring anneal.

EXAMPLE 6

[0037] A copper - 0.59% magnesium alloy was given a restructuring anneal following initial rod rolling in a manner after Example 1. The annealed wire was then drawn to 0.004 inch diameter in several steps. The resultant properties are shown in Table 4, below.

TABLE 4

Diameter, inch	Reduction in Area, %	Tensile Strength, ksi	Electrical Conductivity, % IACS
0.0874	92.1	100.3	64.5
0.0359	98.7	119.9	64.9
0.0145	99.78	132.8	62.3
0.0040	99.98	160.0	61.4

The 160 ksi tensile strength is very high for a copper alloy with an electrical conductivity of greater than 60% IACS. Indeed, this represents a unique combination of tensile strength and electrical conductivity for a copper alloy. Although the electrical conductivity of this alloy is less than that of copper-cadmium, the combination of properties is excellent and is quite useful.

EXAMPLE 7

[0038] A copper - 0.12% magnesium - 0.1% tin - 0.02% phosphorus was given a restructuring anneal of the present invention in accordance with the procedure of Example 1. The alloy was annealed following initial rod rolling, the annealed wire was then drawn to a 0.004 inch diameter in several steps and the resultant properties shown in Table 5, below.

TABLE 5

Diameter, inch	Reduction in Area, %	Tensile Strength, ksi	Electrical Conductivity, % IACS
0.3117	0.0	39.2	81.9
0.2573	31.9	56.8	81.7
0.2159	52.0	64.8	80.8
0.1921	62.0	66.4	80.8
0.1715	69.7	70.2	
0.1583	74.2	68.7	80.9
0.1441	78.6	71.4	80.7
0.1203	85.1	74.9	81.4
0.1010	89.5	77.5	81.1
0.0359	98.7	91.4	78.9
0.0145	99.78	108.6	77.1
0.0040	99.98	128.8	74.4

The alloy could easily be drawn to 0.004 inch diameter. The results shown in Table 5 clearly indicate that at 0.004 inch diameter a significant improvement in tensile strength is obtained.

EXAMPLE 8

[0039] In accordance with this example a 19/38 AWG conductor was made using the single end 0.004 inch diameter wire obtained in Example 7. This conductor was tested to determine its flex life according to the procedure outlined in ASTM B470. Flex life of this conductor, as shown in Table 5, below, was superior to that of copper - 1% cadmium and a base copper - 0.15% magnesium which was processed with the restructuring anneal of the present invention.

TABLE 6

	Cu-1%Cd	Cu-0.15%Mg	Cu-0.12%Mg-0.1%Sn-0.02%P
Break Load, 1b	30.9	28.0	29.4
Single End Size, inch	0.0041	0.0040	0.0040
Flex Life	23,617	35,038	45,738

[0040] While the present invention has been described in the context of single end wires, it should be recognized that the invention is applicable to and covers cables formed from multiple wires processed in accordance with the techniques described hereinbefore. It is to be understood that the invention is not limited to the illustrations described and shown herein, which are deemed to be merely illustrative of the best modes of carrying out the invention, and which are susceptible of modification of form, size, arrangement of parts and details of operation. The invention rather is intended to encompass all such modifications which are within its spirit and scope.

Claims

1. A copper alloy wire having high strength and high conductivity which comprises a copper alloy containing from 0.05 to 0.9 wt% magnesium and more than 15 ppm impurities in total, said wire having a single end diameter less than 0.010 inches, a tensile strength of at least 100 ksi, and an electrical conductivity greater than 60% IACS.

2. A copper alloy wire according to claim 1, wherein said tensile strength is at least 110 ksi.

3. A copper alloy wire according to claim 1, wherein said electrical conductivity is greater than 70% IACS.

4. A copper alloy wire according to claim 1, wherein said copper alloy also contains from 0.01 to 0.3 wt% phosphorous.

5. A copper alloy wire according to claim 4, wherein said phosphorous is present in an amount from 0.01 to 0.15 wt% and said magnesium is present in an amount from 0.1 to 0.4 wt%.

6. A copper alloy wire according to claim 4, wherein a majority of particles of said phosphorous are submicron in size.

7. A copper alloy wire according to claim 1, wherein said copper alloy also contains at least one additional constituent selected from the group consisting of from 0.01 to 1.0 wt% iron, from 0.01 to 0.5 wt% nickel, from 0.01 to 0.3 wt% phosphorous, from 0.01 to 0.2 wt% silver, from 0.01 to 0.2 wt% tin, and from 0.01 to 0.5 wt% zinc.

8. A copper alloy wire according to claim 7, wherein said at least one additional constituent includes iron in an amount from 0.01 to 0.5 wt%.

9. A copper alloy wire according to claim 7, wherein said at least one additional constituent includes tin in an amount from 0.01 to 0.1 wt%.

10. A copper alloy wire according to claim 7, wherein said at least one additional constituent includes phosphorous in an amount from 0.02 to 0.15 wt%.

11. A copper alloy wire according to claim 1, wherein said wire is in a restructuring annealed and cold worked condition.

12. A copper alloy wire according to claim 1, wherein said single end diameter is greater than 0.002 inches.

13. A copper alloy having high strength and high conductivity which comprises a copper alloy consisting of from 0.05 to 0.9 wt% magnesium, 0.01 to 0.3 wt% phosphorous, and the balance copper and more than 15 ppm impurities in total, said wire having a single end diameter no greater than 0.010 inches, a tensile strength of at least 100 ksi, and an electrical conductivity greater than 70% IACS.

14. A copper alloy according to claim 13, wherein said phosphorous content is in the range of from 0.01 to 0.15 wt%, and said tensile strength is at least 110 ksi.

15. A copper alloy wire having high strength and high conductivity which comprises a copper alloy consisting of from 0.05 to 0.9 wt% magnesium, at least one constituent selected from the group consisting of from 0.01 to 1.0 wt% iron, from 0.01 to 0.5 wt% nickel, from 0.01 to 0.3 wt% phosphorous, from 0.01 to 0.2 wt% silver, from 0.01 to 0.2 wt% tin, and from 0.01 to 0.5 wt% zinc, and the balance copper and more than 15 ppm impurities in total, said wire having a single end diameter no greater than 0.010 inches, a tensile strength of at least 100 ksi, and an electrical conductivity greater than 70% IACS.

16. A process for manufacturing a copper alloy wire having high strength and high conductivity comprising the steps of:

providing a base material formed from a copper alloy containing from 0.05 to 0.9 wt% magnesium and more than 15 ppm impurities in total;

cold working said base material into a wire having at least a 40% reduction in original cross section area;

performing a restructuring anneal after said cold working step; and

cold working said annealed material into a wire having a final gage of no greater than 0.010 inches.

17. A process according to claim 16, wherein said restructuring anneal is performed after said base material has been cold worked into a wire having at least a 70% reduction in said original cross section area.

18. A process according to claim 16, wherein said restructuring anneal is performed at a temperature in the range of 650 to 1050°F for a time period in the range of 1 to 5 hours.

19. A process according to claim 18, wherein said restructuring anneal is performed at a temperature in the range of 750 to 900°F for a time period in the range of 2 to 3 hours.

20. A process according to claim 16, wherein said base material providing step comprises providing material formed from a copper alloy consisting of from 0.05 to 0.9 wt% magnesium and the balance copper and more than 15 ppm impurities in total.

21. A process according to claim 16, wherein said base material providing step comprises providing material formed from a copper alloy consisting of from 0.05 to 0.9 wt% magnesium, from 0.01 to 0.3 wt% phosphorous, and the balance copper and more than 15 ppm impurities in total.

22. A process according to claim 16, wherein said base material providing step comprises providing material formed from a copper alloy consisting of from 0.05 to 0.9 wt% magnesium, at least one constituent selected from the group consisting of from 0.01 to 1.0 wt% iron, from 0.01 to 0.5 wt% nickel, from 0.01 to 0.3 wt% phosphorous, from 0.01 to 0.2 wt% silver, from 0.01 to 0.2 wt% tin, and from 0.01 to 0.5 wt% zinc, and the balance copper and more than 15 ppm impurities in total.

23. A process according to claim 16, wherein said final gage cold working step comprises cold working said annealed material into a wire having a diameter less than 0.010 inches.

24. A non-cadmium containing copper alloy wire having high strength and high conductivity which comprises a copper alloy containing from 0.05 to 0.9 wt% magnesium and more than 15 ppm impurities in total, said single end wire having a diameter no greater than 0.10 inches, a tensile strength of at least 100 ksi, and an electrical conductivity greater than 60% IACS.

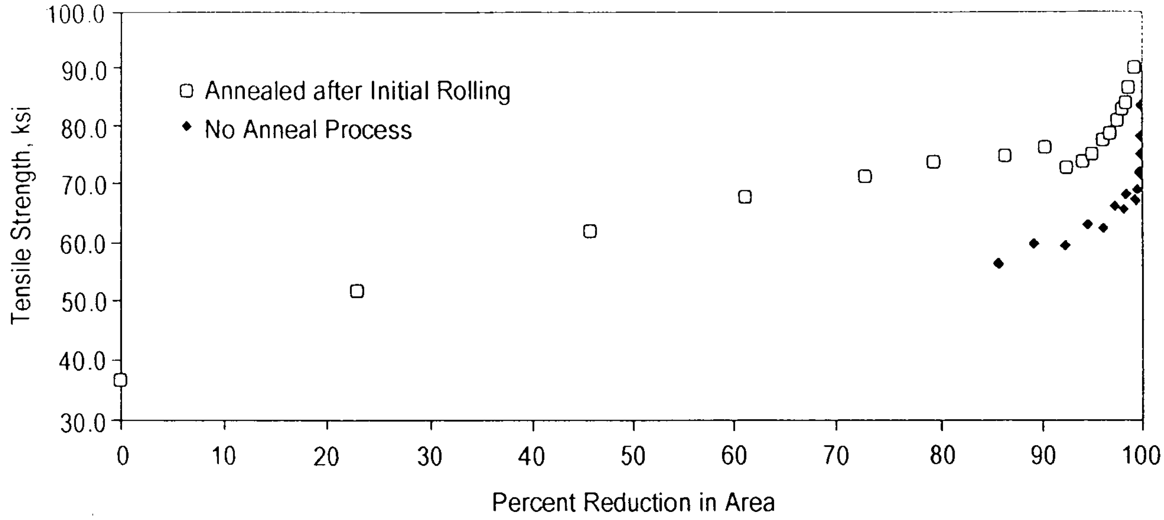
Tensile Strength, ksi
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
Annealed after Initial Rolling
No Anneal Process
0
10
20
30
40
50
60
70
80
90
100
Percent Reduction in Area

FIG. 1

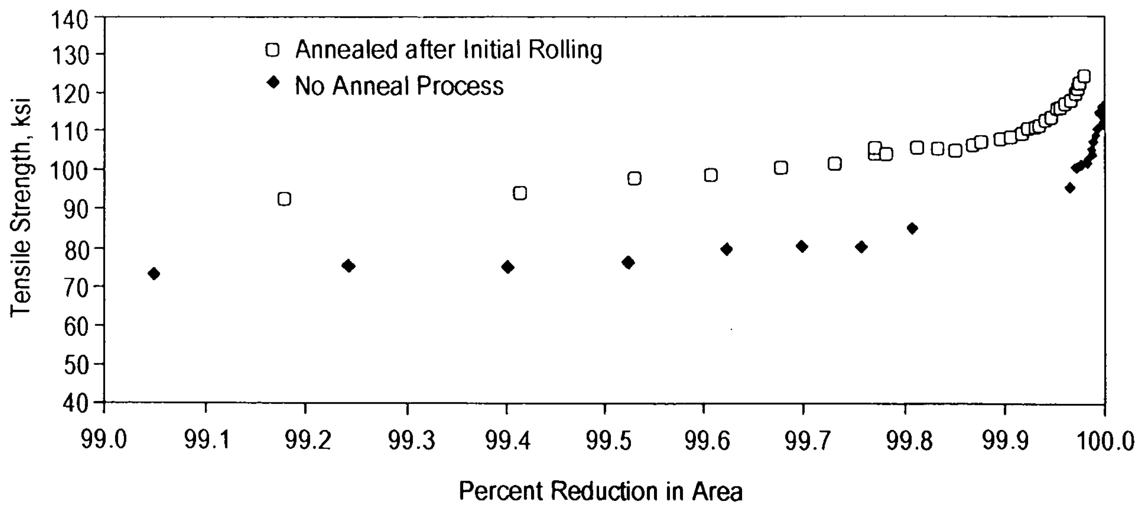
Tensile Strength, ksi
140
130
120
110
100
90
80
70
60
50
40
Annealed after Initial Rolling
No Anneal Process
99.0
99.1
99.2
99.3
99.4
99.5
99.6
99.7
99.8
99.9
100.0
Percent Reduction in Area

FIG. 2

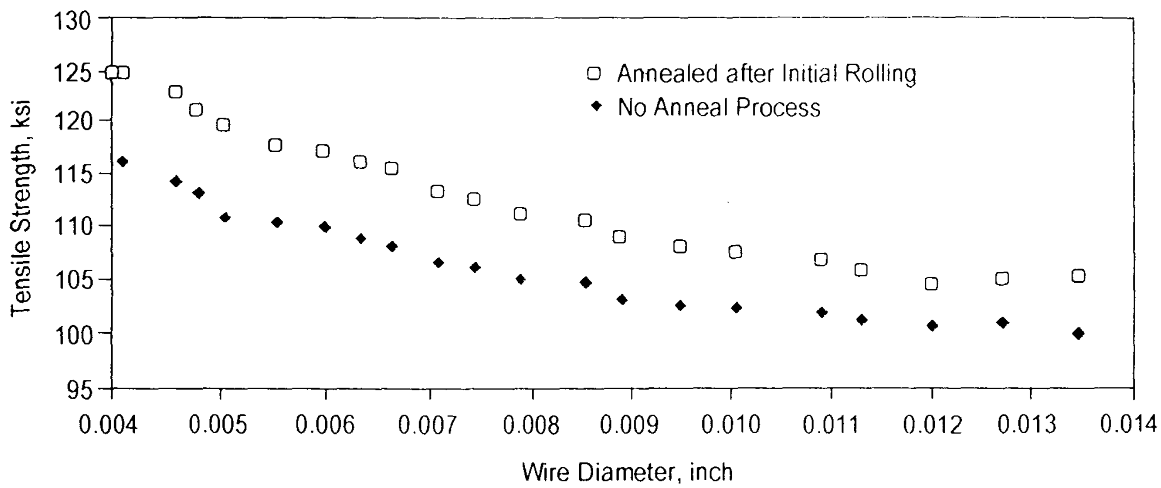
Annealed after Initial Rolling
No Anneal Process
Tensile Strength, ksi
130
125
120
115
110
105
100
95
0.004
0.005
0.006
0.007
0.008
0.009
0.010
0.011
0.012
0.013
0.014
Wire Diameter, inch

FIG. 3

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 29 2667

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	PATENT ABSTRACTS OF JAPAN vol. 015, no. 229 (E-1076), 11 June 1991 (1991-06-11) -& JP 03 067401 A (FURUKAWA ELECTRIC CO LTD:THE), 22 March 1991 (1991-03-22)	1-10, 13-15,24	C22C9/00 C22F1/08
A	* abstract *	11,12, 16-23	

X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 128 (C-1174), 2 March 1994 (1994-03-02) -& JP 05 311283 A (MITSUBISHI SHINDOH CO LTD), 22 November 1993 (1993-11-22)	1-7,10, 11, 13-15,24	
A	* abstract *	8,9,12, 16-23	

X	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 13, 30 November 1998 (1998-11-30) -& JP 10 219372 A (KOBE STEEL LTD), 18 August 1998 (1998-08-18)	1-7, 9-11, 13-15,24	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
A	* abstract *	8,12, 16-23	C22C C22F

X	US 3 677 745 A (FINLAY WALTER L ET AL) 18 July 1972 (1972-07-18)	1-7,10, 13-15,24	
A	* claims 1-10 *	8,9,11, 12,16-23	
	* examples 1-4 *		

X	WO 99/05331 A (OLIN CORP) 4 February 1999 (1999-02-04)	1-11, 13-15,24	
A	* claims 1-17 *	12,16-23	

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23 September 2004	Vlassi, E

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 29 2667

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
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