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(56) References cited:  
**GB-A- 536 893 SU-A- 430 176**  
**SU-A- 544 698 US-A- 2 809 889**  
**US-A- 4 818 307 US-A- 4 883 112**

• **PATENT ABSTRACTS OF JAPAN** vol. 1996, no. 05, 31 May 1996 (1996-05-31) -& JP 08 027531 A (SUMITOMO ELECTRIC IND LTD), 30 January 1996 (1996-01-30)  
• **T.B. MASSALSKI, ED.:** "Binary Alloy Phase Diagrams Volume 1" 1990, ASM INTERNATIONAL, OHIO, USA, XP002291612 ISBN: 0-87170-404-8 \* pages 474-476 \*\* pages 498-500 \*\* pages 123-125 \*  
• **DATABASE INSPEC [Online] THE INSTITUTION OF ELECTRICAL ENGINEERS, STEVENAGE, GB;** SOUPTEL D ET AL: "Crystal growth of MgB/sub 2/ from Mg-Cu-B melt flux and superconducting properties" XP002291674 Database accession no. 7634756 -& JOURNAL OF ALLOYS AND COMPOUNDS, vol. 349, no. 1-2, 3 February 2003 (2003-02-03), pages 193-200, XP004400109 SWITZERLAND ISSN: 0925-8388  
• **PATENT ABSTRACTS OF JAPAN** vol. 1998, no. 11, 30 September 1998 (1998-09-30) -& JP 10 158766 A (MIYOSHI GOKIN KOGYO KK), 16 June 1998 (1998-06-16)

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- PATENT ABSTRACTS OF JAPAN vol. 1996, no. 11, 29 November 1996 (1996-11-29) -& JP 08 174272 A (MITSUI MINING & SMELTING CO LTD), 9 July 1996 (1996-07-09)

**Description**

## BACKGROUND OF THE INVENTION

5 Field of the Invention

**[0001]** The present invention relates to lead frames, optical communication connector cases, optical amplifier cases, and heat sinks for semiconductor devices.

10 **[0002]** Priority is claimed on Japanese Patent Application No. 2003-124746, filed April 30, 2003, the content of which is incorporated herein by reference.

## Description of Related Art

15 **[0003]** The material conventionally used for lead frames for integrated circuit devices and so forth is, for example, an Fe-Ni alloy or a Cu alloy which has comparable of thermal expansion coefficients as that of Si as a material for device. Cu, Al, Au, Mo, and their alloys or Cu-W alloys and Cu-Mo alloys which are excellent in thermal conductivity are used as materials for a heat sink which dissipates the heat generated from a CPU (Central Processing Unit), and which are provided inside or outside of the package of a personal computer (refer to Japanese Unexamined Patent Application, First Publication No. Hei 10-8166, pages 2 to 3). In this reference patent, a copper alloy to which is added 10 to 30%  
20 by weight of Cr, and which made the thermal expansion coefficient of the copper alloy approximate that of a semiconductor device, and which was improved the strength, is disclosed. Moreover, Cu or Cu alloys, Al, Mo, Cu-W alloys or Cu-Mo alloys and so forth are used for the material for connector cases of optical communication and optical amplifier cases, in the reference.

25 SUMMARY OF THE INVENTION

**[0004]** With the miniaturization and integration of electronic device such as personal computers, cellular phones, and optical devices, heat generation during operation of the devices has become more of a problem in recent years, and therefore the problem describe below occurs in the prior art.

30 **[0005]** In order to prevent distortions between a device and a lead frame by heat, and a bad connection, a material which has almost the same thermal expansion coefficient as a material for device such as Si and which is capable of dissipating the generated heat, is required as a material for a lead frame. A Fe-Ni alloy which is used conventionally has low thermal conductivity and is insufficient at dissipating the heat. Although Cu or conventional Cu alloy has high thermal conductivity, it is distorted by heat due to a higher heat expansion coefficient than a material for device.

35 **[0006]** Furthermore, due to the trend of replacing the conventional plastics package material of the semiconductor device with one of ceramics because of higher integration and greater speed in the future, a material which has good thermal conductivity for dissipating heat as a heat sink material, and has comparable thermal expansion coefficient as the ceramics to be used in the package, is required. However, Al, Cu, and conventional Cu alloys have a problem in packages made from ceramics since Al, Cu, and conventional Cu alloys have higher thermal expansion coefficients  
40 than ceramics packages, although they have high thermal conductivity. On the other hand, Cu-W alloys, Cu-Mo alloys, and so forth have high thermal conductivity and lower thermal expansion coefficients than conventional Al, Cu, and Cu alloys, and it is thereby possible to approximate the thermal expansion coefficient of these alloys to that of ceramics; however, these alloys are expensive. If elemental Mo is used, it is expensive and is difficult to machine to form a heat sink due to the high strength.

45 **[0007]** In addition, a material having a comparable thermal expansion coefficient to that of glass, and having superior heat dissipating properties in order to prevent the shift of light paths inside and wavelength variations of lasers due to temperature variations, is required for connector cases of optical communication or optical amplifier cases. However conventional Al and Cu are insufficient since the thermal expansion coefficients thereof are high. On the other hand, the above Cu-W alloys and Cu-Mo alloys are superior in their properties; however, W and Mo as raw materials  
50 are very expensive and thereby increase material costs. These Cu-W alloys and Cu-Mo alloys are generally manufactured by an infiltration method in which powders of W and Mo are sinter molded to be sponge-like, and the sponge-like W and Mo are impregnated with molten Cu, since W and Mo have high melting point, and W and Mo do not react each other. However, the impregnation is technically difficult and process yield is low, and then the manufacturing cost is increased. Furthermore, in the case of use of elemental Mo, it is expensive and it is difficult to machine it to form a heat sink due  
55 to the high strength thereof.

**[0008]** From document JP-A-08027531 and T.B. Massalki, Ed Binary Alloy Phase Diagrams, Volume 1, page 474-476, a binary Alloy Cu-B and its use for electronic equipments is known. Document US-2809889 discloses an aluminum bronze alloy containing 12 to 15 % of aluminum, 12 to 15 % of nickel, 2 to 3 % of B, and the balance Cu. From document

Souptel D. et.al. - Crystal growth of MgB<sub>2</sub> from Mg-Cu-B melt flux and superconducting properties, Journal of Alloys and Compounds, vol. 349, no. 1-2, p. 193-200, a Mg-Cu-B alloy is known and in this document the effects of superconductivity of Mg-B at an extremely low temperature are described.

**[0009]** US 4818307 discloses a Cu alloy with a dispersion of hard particles of silicides further composed with borides of Fe-Ni in complex form. The Cu alloy is directed to a wear resistant material.

**[0010]** The present invention was made in view of these problems. An object of the present invention is to provide a copper alloy which has superior thermal conductivity which is comparable to that of the conventional material, a lower thermal expansion coefficient than conventional copper, and is capable of being produced at a lower cost.

**[0011]** These objects are achieved by a copper alloy according to claim 1. Preferred embodiments of the inventive copper alloy are stated in the subclaims.

**[0012]** The first aspect of the present invention is a copper alloy comprising B at 0.01 to 10.0 % by weight, and at least one element selected from the group of Ni, Co, Al, Si, Fe, Zr, and Mn at 0.05 to 40.0 % by weight in total amount, the balance containing Cu and inevitable impurities, and total volume ratio of elemental B and an intermetallic compound of B with at least one element selected from the group of Cu, Ni, Co, Al, Si, Fe, Zr, and Mn at 1 to 80 % by volume based on total volume, and the content of A1 by weight is not more than 10 times the weight of B.

**[0013]** In the present invention, by adding B and at least one element selected from the group of Ni, Co, Al, Si, Fe, Zr, and Mn to Cu, a group of intermetallic compounds comprising B elemental phase, Cu-B alloy phase, Cu-X-B alloy phase, and X-B alloy phase all having low thermal expansion coefficients are formed in Cu, and this compound becomes a copper alloy having high thermal conductivity and low thermal expansion coefficient. Here, X represents at least one element selected from the group of Ni, Co, Al, Si, Fe, Zr, and Mn. Since Al is included in the alloy, by controlling the content of Al to be no more than 10 times that of B, the thermal expansion coefficient is prevented from becoming high by using Al having a high thermal expansion coefficient.

**[0014]** The above copper alloy comprising B at 0.1 to 9.8 % by weight, and 0.5 to 40.0 % by weight in total of at least one element selected from the group of Ni, Co, Al, Si, Fe, Zr and Mn, and the balance containing Cu and inevitable impurities, and the total volume ratio of an elemental B and an intermetallic compound of B with at least one element selected from the group of Cu, Ni, Co, Al, Si, Fe, Zr, and Mn at 3.0 to 74.5 % by volume based on total volume, is preferable.

**[0015]** When the above copper alloy includes Al, for example, Al-B intermetallic compound is formed. The above copper alloy of the present invention does not exhibit high thermal expansion coefficient since the Al-B intermetallic compound has low thermal expansion coefficient, even though the Al having a high thermal expansion coefficient is used.

**[0016]** Furthermore, the copper alloy of the present invention is, for example, manufactured by a casting process or powder sintering method.

**[0017]** According to the present invention, by adding B, at least one selected from the group of Ni, Co, Al, Si, Fe, Zr, and Mn to Cu, a copper alloy having high thermal conductivity and low thermal expansion coefficient due to the group of intermetallic B compounds having low thermal expansion coefficient, is formed in Cu. B forms intermetallic compounds reacting with other elements easily, and it allows production of an alloy by the casting process from molten metal or the powder sintering method, and thereby the production cost can be reduced.

#### DETAILED DESCRIPTION OF THE INVENTION

**[0018]** Below, the copper alloy of the present invention will be explained in detail. The inventors of the present application discovered that Cu-X-B alloy are effective materials to solve the problem. Here, X represents at least one element selected from the group of Ni, Co, Al, Si, Fe, Zr, and Mn. The copper alloy of the present invention has superior thermal conductivity and electrical conductivity comparable to that of the conventional copper alloy and has lower thermal expansion coefficient than copper. Specifically, a copper alloy which is in the state including copper at no less than 20 % by volume, has high thermal conductivity no less than 100W/m·K, and this results in superior performance comparable to that of Cu-W alloy, Mo and so forth, in applications which require dissipating heat.

The copper alloy in the present invention may be produced by the casting process since the melting temperature decreases by the interaction between B or X and Cu, and by forming intermetallic compound of X and B, although B or X have high melting temperature. Furthermore, the copper alloy in the present invention may be produced by the powder sintering method in the case in which the component segregates inside the alloy material by using a casting process. In this powder sintering method, the copper alloy in the present invention may be produced at low sintering temperature since B or X reacts with Cu. The copper alloy in the present invention is produced inexpensively in comparison with Cu-W alloys and Cu-Mo alloys which are produced by an infiltration method since the copper alloy of the present invention is easier to solid-disperse in Cu with a phase comprising other elements than is the conventional copper alloy.

**[0019]** Next, the reasons for the limitation of each component in the copper alloy of the present invention are explained.

B: from 0.01 to 10.0% by weight

**[0020]** B has a low thermal expansion coefficient, and when B is added to Cu, a phase having a low thermal expansion coefficient in Cu is formed. B is easy to mix or chemically combine with other elements, and the phase including B is thereby easy to disperse into Cu. Accordingly, by adding B to Cu, a copper alloy having low thermal expansion coefficient and homogeneous characteristics can be obtained. If the content of B is less than 0.01 % by weight, the thermal expansion coefficient and thermal conductivity are comparable to those of Cu and no effect of further addition could be obtained. On the other hand, if the content of B is more than 10.0 % by weight, the deviation of thermal expansion coefficient in each production lot become big and difficult to handle because of the brittleness of the material. It is preferable that the content of B be from 0.1 to 8.1 % by weight and that the content of volume ratio of elemental B and Cu-B intermetallic compound be from 0.6 to 39.0 % by volume.

**[0021]** Ni, Co, Al, Si, Fe, Zr, and Mn: total amount is from 0.05 to 40.0 % by weight

**[0022]** Si, and Zr easily form a compound phase with Cu. Cu alloys according to the present invention exist in the state of intermetallic compounds of Al, Si, and Zr with Cu, which includes B. If the content of Si, or Zr is less than 0.05 % by weight, the advantage of addition could not be obtained since the thermal expansion coefficient and thermal conductivity are comparable to that of copper. On the other hand, if the content of any of these elements is more than 40.0 % by weight, cracks occur and the compact is difficult to use as a compact. Co and Fe are elements which do not solid disperse with Cu; however, in the copper alloy of the present invention, Co and Fe form intermetallic compounds having low thermal expansion coefficients by bonding B, and they maintain the state of intermetallic compounds. The intermetallic compounds comprising B and Co and/or Fe, has a lower melting point than elements in the elemental state and thereby the intermetallic compound melts at a lower temperature, the segregation while casting and fine dispersion is performed. Elemental Ni is solid dispersible with Cu; however, Ni-B alloy compounds do not significantly solid disperse with Cu and thereby Ni-B-Cu alloy behave in the same ways as the above Co and Fe-B alloy compounds. At this time, when the addition amount of Co, Fe, and Ni is less than 0.05% by weight, the thermal expansion coefficient does not decrease. When the addition amount of Co, Fe, and Ni is more than 40.0 % by weight, dispersion to Cu is insufficient and thereby cracking of the compact tends to occur while molding in a casting process or powder sintering method. In the copper alloy according to the present invention, it is preferable that the content of B be from 0.1 to 9.8 % by weight and that the total content of at least one element selected from the group of Ni, Co, Al, Si, Fe, Zr, and Mn be at 0.5 to 40.0 % by weight.

**[0023]** Total amount of elemental B, and intermetallic compound of B with at least one element selected from Cu, Ni, Co, Al, Si, Fe, Zr and Mn: from 1.0 to 80.0 % by volume.

**[0024]** When the total volume ratio of elemental B, and intermetallic compound of B with at least one element selected from Cu, Ni, Co, Al, Si, Fe, Zr and Mn is less than 1.0 % by volume, the thermal expansion coefficient of the alloy decreases insufficiently in comparison with that of Cu. When the volume content ratio of elemental B, and intermetallic compound of B with at least one element selected from Cu, Ni, Co, Al, Si, Fe, Zr, and Mn is more than 80.0 % by volume, the thermal conductivity falls below 100 W/m-K which is the value comparable to those of Cu-W alloys, Mo, and so forth. In the copper alloy according to the present invention, the total volume ratio of the intermetallic compound of Cu with elemental B, and at least one element selected from the group of Ni, Co, Al, Si, Fe, Zr, and Mn is from 3.0 to 74.5 % by volume in total volume.

**[0025]** The content of Al: 10 times or less of the content of B (mass ratio)

**[0026]** Al as an element has as high a thermal expansion coefficient as Mg; however, the thermal expansion coefficient decreases by bonding B and by forming Al-B intermetallic compounds. In the case of adding Al, the content of Al in copper alloy is controlled to be 10 times or less of the content of B in mass ratio. When the ratio of Al is higher than 10 times of B in mass ratio, an Al phase having a high thermal expansion coefficient is formed, and the thermal expansion coefficient become higher than that of Cu.

**[0027]** Next, the production method of the copper alloy of the present invention will be explained. The copper alloy of the present invention is produced by the casting process or the powder sintering method. In the case of producing by the casting process, for example, Cu or the raw material of Cu-B and Ni-B is melted and cast by the high-frequency melting method. In these processes, the melting temperature and the controlling of atmosphere and so forth are timely adjusted depending on the material used. After soaking at 600 to 1000°C, a hot rolling, a cold strip, and other processes are performed, and the alloy is molded to a predetermined shape. In the case in which the above casting process has problems of the occurrence of cracks in the compact or the unsatisfactory dispersion of the added elements, the alloy may be produced by the powder sintering method. In the method of sintering, Cu or Cu-B powder, and at least one element selected from Ni, Co, Al, Si, Fe, Zr, and Mn, and powder produced from these element and B are mixed to be a objective component and a mold of predetermined shape is used and these powder are sintered at 600 to 900°C in an inert gas. The above powder sintering method is preferably applied when the content of B is at least 5 % by weight or the content of other added elements is at least 20% by weight.

**[0028]** The copper alloy according to the present invention is processed to form lead frames, optical communication connector cases, and heat sinks for semiconductor devices and so forth. These compact using the copper alloy according to the present invention have lower thermal expansion coefficient than that of the compact using copper, and the electrical

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conductivity and thermal conductivity are superior to those of the conventional compact using Fe-42Ni and so forth. The copper alloy according to the present invention has at least 100 W/m·K (approximately 1/4 of that of Cu) of thermal conductivity at the same level of those of Cu-W alloy, Mo, and so forth which are used for the conventional optical communication connector cases, heat sinks for semiconductor devices, and so forth. The copper alloy of the present invention can be provided at lower cost than these alloys.

**[0029]** In a copper alloy according to the present invention, by adding B, and at least one element selected from a group of Ni, Co, Al, Si, Fe, Zr, and Mn to Cu, B group intermetallic compound having low thermal expansion coefficient in Cu is formed, thereby the material having low thermal expansion coefficient can be produced while maintaining high thermal conductivity which is a feature of the copper alloy. Since B easily generates intermetallic compounds reacting with other elements, the copper alloy can be produced by a casting process from molten metal which is a relatively easy method. The copper alloy of the present invention can be produced by the powder sintering method. The copper alloy can be produced at lower cost than Cu-W alloys, Cu-Mo alloys, and so forth those are produced by special production methods such as the infiltration method. By selecting low-cost B compounds which are added to the alloy, the raw material cost can be reduced.

### Examples

**[0030]** Below, examples of the present invention are explained in comparison with comparative examples which are outside the range of the present invention. In the first reference examples of the present invention, oxygen free copper or base material of Cu-B alloy and so forth were melted in vacuo by using the high-frequency melting method and B in an amount, was added to the above molten metal. This molten metal with B was cast into an ingot of 12 mm square, heated at 600 to 900°C for 1 hour, and rolled to be 3 mm plate by hot rolling. After these steps, heat treatment at 600 to 900°C was provided and the alloy plate was processed into a test piece having a shape required for the measurement, and the copper alloy samples of Reference Example 1 and Reference Example 2 were obtained. After mixing the powder B and powder of Cu or Cu-B wherein the content of powder B is shown in Table 1, the mixture was sintered at 600 to 1000°C in inert gas. After this sintered body was processed to a test piece, the shape of which is required for the measurement, a heat treatment at 600 to 900°C was provided, and processed into a copper alloy sample of Reference Example 3. In the same process as Reference Example 3, a copper alloy sample of Comparative Example 1 in which the B content is higher than that of the Reference Examples 1 to 3 was obtained.

**[0031]** The thermal expansion coefficient and thermal conductivity were measured for the above copper alloys of Reference Examples 1 to 3, the copper alloy of Comparative Example 1, Cu (Comparative Example 2), Mo (Comparative Example 3) and Fe-42Ni (Comparative Example 4). The thermal expansion coefficient was measured by a differential transformer method within the range from 20 to 150°C, and the average was taken. The thermal conductivity was measured in accordance with Japanese Industrial Standard JIS-A1412, at 25°C. The volume content was calculated from data measured from phase areas of B or phase areas including B, based on the total area, by taking some photos at 100 to 400 magnification of each sample. These results are shown in Table 1.

Table 1

	Alloy component	Component weight ratio (wt%)		Content of B and B intermetallic compound (vol %)	Thermal expansion coefficient (×10 <sup>6</sup> /K)	Thermal conductivity (W/m·K)
		B	Balance			
Reference Example 1	Cu- B	0.17	Cu+ inevitable impurities	0.6	16.7	362
Reference Example 2	Cu-B	1.96		14.5	15.7	216
Reference Example 3	Cu-B	8.06		38.3	13.0	128
Comparative Example 1	Cu-B	16.34		82.5	8.4	72
Comparative Example 2	Cu	0.00		0.0	17.3	395

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(continued)

	Alloy component	Component weight ratio (wt%)		Content of B and B intermetallic compound (vol %)	Thermal expansion coefficient ( $\times 10^6/K$ )	Thermal conductivity (W/m·K)
		B	Balance			
Comparative Example 3	Mo	-	-	-	5.1	138
Comparative Example 4	Fe-42Ni	-	-	-	4.2	17

**[0032]** As shown in Table 1, copper alloys of Reference Examples 1 to 3 have a thermal expansion coefficient lower than that of Cu, and a thermal conductivity higher than 100 W/m·K. In contrast, the copper alloy of Comparative Example 1 whose ratio of elements except Cu by volume is higher than the range according to the present invention, have a thermal conductivity lower than 100 W/m·K and sufficient heat dissipation cannot be expected. The copper alloy of the Comparative Example 1 is produced by the powder sintering method, the sintered body was extremely brittle and difficult to handle.

**[0033]** In the first examples of the present invention, copper alloys of Example 7 to 36 and Reference Examples 4 to 6 which are within the range of the present invention by the same process as the Reference

**[0034]** Example 1 to 3 using the casting process or the powder sintering method and copper alloys of Comparative Example 5 to 13, which are outside range of the present invention, are produced. In the casting process, the high frequency melting method was employed. The oxygen free high conductivity copper, base material of Cu-B alloy, and so forth were melted to a molten state in vacuo or in an Ar atmosphere, B and at least one element selected from Mg, Ni, Co, Al, Si, Fe, Zr, and/or Mn was added to the molten metal wherein the content of each element or the alloy of Ni-B, Fe-B, Cu-Mg, and so forth becoming the predetermined content. This is cast into an ingot of 12 mm square, and heated at 600 to 900°C for 1 hour, and the cast was rolled to be 3 mm plate by hot rolling. After these steps, heat treatment at 600 to 900°C was provided and processed into a test piece having a shape which is required for the measurement. On the other hand, in the case of the powder sintering method, an X powder from B and at least one element selected from Mg, Ni, Co, Al, Si, Fe, Zr, and/or Mn was prepared. After mixing X powder, Cu or powder of Cu-B in the predetermined content of each element to be added, the mixed powder was sintered at 600 to 1000°C in an inert gas. The sintered body was processed to a test piece having a shape which is required for the measurement, and a heat treatment at 600 to 900°C was provided.

**[0035]** The thermal expansion coefficient, thermal conductivity, and volume ratio were measured, using the same method as for the above Reference examples, for the copper alloys of Examples 7 to 36 and Reference Examples 4 to 6 and Comparative Examples 5 to 13, which were produced by the above process. The results are shown in Tables 2 to 4. In the component weight ratio of Tables 2 to 4, the balance is Cu and inevitable impurities.

Table 2

	Alloy component	Component weight ratio (wt%)									Content of B and B intermetallic compound (vol %)	Thermal expansion coefficient ( $\times 10^6/K$ )	Thermal conductivity (W/m·K)
		B	Mg	Ni	Co	Al	Si	Fe	Zr	Mn			
Reference Example 4	Cu-Mg-B	1.48	0.91	-	-	-	-	-	-	-	9.3	14.4	370
Reference Example 5	Cu-Mg-B	1.48	1.64	-	-	-	-	-	-	-	12.4	15.1	360
Reference Example 6	Cu-Mg-B	1.81	1.97	-	-	-	-	-	-	-	14.8	14.8	337
Example 7	Cu-Si-B	1.88	-	-	-	-	0.49	-	-	-	8.1	13.5	333
Example 8	Cu-Si-B	2.57	-	-	-	-	3.74	-	-	-	19.5	13.3	198
Example 9	Cu-Zr-B	0.85	-	-	-	-	-	-	1.32	-	4.9	14.1	350
Example 10	Cu-Zr-B	2.19	-	-	-	-	-	-	7.60	-	20.1	11.4	240
Example 11	Cu-zr-B	6.31	-	-	-	-	-	-	25.50	-	69.1	9.4	125
Example 12	Cu-Co-B	0.17	-	-	2.34	-	-	-	-	-	3.0	14.8	356
Example 13	Cu-Co-B	0.89	-	-	4.86	-	-	-	-	-	7.9	13.3	317
Example 14	Cu-Co-B	5.59	-	-	21.53	-	-	-	-	-	36.5	13.0	250
Example 15	Cu-Co-B	9.76	-	-	39.15	-	-	-	-	-	60.4	10.1	130
Example 16	Cu-Al-B	1.89	-	-	-	1.42	-	-	-	-	10.7	14.4	315
Example 17	Cu-Al-B	1.44	-	-	-	10.27	-	-	-	-	30.8	15.4	165
Example 18	Cu-Al-B	9.49	-	-	-	28.10	-	-	-	-	72.4	14.6	108
Example 19	Cu-Fe-B	1.77	-	-	-	-	-	2.30	-	-	8.8	14.1	329
Example 20	Cu-Fe-B	3.23	-	-	-	-	-	10.49	-	-	23.7	11.3	216
Example 21	Cu-Fe-B	9.70	-	-	-	-	-	39.53	-	-	70.3	8.9	115

Table 3

	Alloy component	Component weight ratio (wt%)									Content of B and B intermetallic compound (vol %)	Thermal expansion coefficient ( $\times 10^6/K$ )	Thermal conductivity (W/m·K)
		B	Mg	Ni	Co	Al	Si	Fe	Zr	Mn			
Example 22	Cu-Ni-B	0.89	-	4.84	-	-	-	-	-	-	7.9	14.1	288
Example 23	Cu-Ni-B	1.29	-	20.95	-	-	-	-	-	-	32.7	13.5	134
Example 24	Cu-Ni-B	2.40	-	13.02	-	-	-	-	-	-	20.4	13.6	195
Example 25	Cu-Ni-B	2.93	-	5.30	-	-	-	-	-	-	22.1	13.6	216
Example 26	Cu-Ni-B	3.78	-	20.53	-	-	-	-	-	-	35.8	13.1	153
Example 27	Cu-Ni-B	5.22	-	38.61	-	-	-	-	-	-	74.2	12.7	120
Example 28	Cu-Mn-B	0.15	-	-	-	-	-	-	-	4.63	6.9	14.0	290
Example 29	Cu-Mn-B	5.22	-	-	-	-	-	-	-	18.30	34.3	13.1	152
Example 30	Cu-Ni-Al-B	2.48	-	7.01	-	2.97	-	-	-	-	36.2	14.5	132
Example 31	Cu-Ni-Al-B	2.95	-	5.33	-	4.89	-	-	-	-	19.3	12.7	190
Example 32	Cu-Ni-Al-B	2.91	-	5.27	-	0.49	-	-	-	-	13.7	13.6	203
Example 33	Cu-Ni-Al-B	3.20	-	15.07	-	6.40	-	-	-	-	45.5	11.9	142
Example 34	Cu-Ni-Si-B	2.40	-	6.25	-	-	0.25	-	-	-	14.8	12.8	200
Example 35	Cu-Ni-Fe-B	3.45	-	6.45	-	-	-	10.02	-	-	43.6	10.9	173
Example 36	Cu-Fe-Zr-B	5.19	-	-	-	-	-	7.63	4.81	-	31.5	12.2	220

Table 4

	Alloy component	Component weight ratio (wt%)									Content of B and B intermetallic compound (vol %)	Thermal expansion coefficient ( $\times 10^6/K$ )	Thermal conductivity (W/m·K)
		B	Mg	Ni	Co	Al	Si	Fe	Zr	Mn			
Comparative Example 5	Cu-Mg-B	0.36	2.85	-	-	-	-	-	-	-	14.1	17.5	316
Comparative Example 6	Cu-Mg-B	0.49	3.27	-	-	-	-	-	-	-	18.9	17.9	297
Comparative Example 7	Cu-Si-B	8.68	-	-	-	-	45.02	-	-	-	Crack	Crack	Crack
Comparative Example 8	Cu-Zr-B	8.41	-	-	-	-	-	-	30.64	-	83.2	8.6	70
Comparative Example 9	Cu-Co-B	11.37 -	-	-	51.42	-	-	-	-	-	85.4	8.2	68
Comparative Example 10	Cu-Al-B	0.80	-	-	-	22.55	-	-	-	-	68.3	17.7	110
Comparative Example 11	Cu-Fe-B	12.10	-	-	-	-	-	52.40	-	-	Crack	Crack	Crack
Comparative Example 12	Cu-Ni <sub>3</sub> B	4.48	-	44.05	-	-	-	-	-	-	86.2	13.7	86
Comparative Example 13	Cu-Fe-Zr-B	7.28	-	-	-	-	-	36.41	7.39	-	Crack	Crack	Crack

[0036] As shown in Tables 2 and 3, the copper alloys of Examples 7 to 36, which are produced within the range of the present invention, have lower thermal expansion coefficients than that of copper and higher thermal conductivities than 100 W/m·K. In contrast, the copper alloy of Comparative Examples 5 and 6, which are outside of the range of the present invention shown in Table 4, have higher thermal conductivity than that of Cu shown in Table 1. This result occurred because Mg, which was solidly dispersed in Cu, makes the thermal expansion coefficient of the alloy high due to the content of Mg being 5 times or more the content of B in mass ratio. In the same manner, the alloy of Comparative Example 10 has a higher thermal expansion coefficient of that of Cu due to the content of Al being 10 times or more than the content of B in mass ratio. In the copper alloy of Comparative Example 8, the content of B and Zr are within the range of the present invention; however, the thermal expansion coefficient of the alloy was lower than that of Cu and the thermal conductivity was under 100 W/m·K due to the volume ratio of B and the intermetallic compound including B exceeded 80 % by volume. In the copper alloys of Comparative Examples 7, 11 and 13, the materials exhibited cracks during the casting process and a test piece for the measurement could not be obtained, even in the powder sintering process, due to the addition content of elements other than B exceeding 40 % by weight. The copper alloys of Comparative Examples 9 and 12 were extremely brittle due to the addition content of the elements other than B exceeding 40 % by weight, and the thermal conductivity was lower than 100 W/m·K due to the volume content of the intermetallic compound exceeding 80 % by volume.

Accordingly, the invention is not to be considered as being limited by the foregoing description, and is only limited by the scope of the appended claims.

## Claims

1. A copper alloy comprising:

0.01 to 10.0 % by weight of B, and  
 at least one element selected from the group of Ni, Co, Al, Si, Fe, Zr, and Mn at 0.05 to 40.0 % by weight in total amount,  
 the balance being Cu and inevitable impurities, and total volume ratio of elemental B and an intermetallic compound of B with at least one element selected from a group of Cu, Ni, Co, Al, Si, Fe, Zr, and Mn is 1 to 80 % by volume based on total volume, and  
 the content of Al by weight is not more than 10 times of the content of B by weight,  
 thermal conductivity of the copper alloy is at least 100 W/m·K, and thermal expansion coefficient of the copper alloy is less than thermal expansion coefficient of Cu ( $17.3 \times 10^{-6}/K$ ).

2. The copper alloy according to claim 1, wherein  
 the content of B is 0.1 to 9.8 % by weight,  
 the content of at least one element selected from the group of Ni, Co, Al, Si, Fe, Zr, and Mn is 0.5 to 40 % by weight in total amount, and the total volume ratio of the element B and the intermetallic compound of B with at least one element selected from the group of Cu, Ni, Co, Al, Si, Fe, Zr, and Mn is 3.0 to 74.5 % by volume based on total volume.

3. The copper alloy according to any one of claims 1 to 2, wherein the alloy is manufactured by a casting process.

4. The copper alloy according to any one of claims 1 to 2, wherein the alloy is manufactured by a powder sintering method.

## Patentansprüche

1. Kupferlegierung, die Folgendes aufweist:  
 0,01 bis 10,0 Gewichtsprozent B, und  
 mindestens ein Element, welches aus der Gruppe bestehend aus Ni, Co, Al, Si, Fe, Zr und Mn besteht, und zwar in einer Menge von 0,05 bis 40 Gewichtsprozent der Gesamtmenge,  
 wobei der Rest Cu und unvermeidbare Verunreinigungen ist, und  
 wobei das Gesamtvolumenverhältnis des Elements B und einer intermetallischen Verbindung von B mit mindestens einem Element, welches aus einer Gruppe bestehend aus Cu, Ni, Co, Al, Si, Fe, Zr und Mn ausgewählt ist, 1 bis 80 Volumenprozent basierend auf dem Gesamtvolumen ist, und  
 wobei der Gewichtsanteil von Al nicht mehr als 10 mal der Gewichtsanteil von B ist,

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wobei die thermische Leitfähigkeit der Kupferlegierung zumindest 100 W/m·K ist, und wobei der thermische Ausdehnungskoeffizient der Kupferlegierung geringer als der thermische Ausdehnungskoeffizient von Cu ( $17,3 \times 10^{-6}/K$ ) ist.

- 5    **2.** Kupferlegierung nach Anspruch 1, wobei  
der Gehalt von B 0,1 bis 9,8 Gewichtsprozent ist,  
wobei der Gehalt von mindestens einem Element, welches aus der Gruppe bestehend aus Ni, Co, Al, Si, Fe, Zr  
und Mn ausgewählt ist, 0,5 bis 40 Gewichtsprozent der Gesamtmenge ist, und  
10 wobei das Gesamtvolumenverhältnis des Elementes B und der intermetallischen Verbindung von B mit mindestens  
einem Element, welches aus der Gruppe bestehend aus Cu, Ni, Co, Al, Si, Fe, Zr und Mn ausgewählt ist, 3,0 bis  
74,5 Volumenprozent basierend auf dem Gesamtvolumen ist.
- 3.** Kupferlegierung nach einem der Ansprüche 1 bis 2, wobei die Legierung durch einen Gussprozess hergestellt wird.
- 15 **4.** Kupferlegierung nach einem der Ansprüche 1 bis 2, wobei die Legierung durch ein Pulversinterverfahren hergestellt  
ist.

### Revendications

- 20 **1.** Alliage de cuivre comprenant :
- 0,01 à 10,0 % en poids de B, et  
au moins un élément choisi dans le groupe Ni, Co, Al, Si, Fe, Zr et Mn à 0,05 à 40,0 % en poids de la quantité totale,  
25 le reste étant constitué de Cu et d'inévitables impuretés, et  
le rapport en volume total de l'élément B et d'un composé intermétallique de B avec au moins un élément choisi  
dans le groupe Cu, Ni, Co, Al, Si, Fe, Zr et Mn est compris entre 1 et 80 % en volume sur la base du volume total, et  
le contenu en Al en poids n'est pas supérieur à 10 fois le contenu en B en poids,  
la conductivité thermique de l'alliage de cuivre est au moins égale à 100 W/m·K, et le coefficient de dilatation  
30 thermique de l'alliage de cuivre est inférieur au coefficient de dilatation thermique du Cu ( $17,3 \times 10^{-6}/K$ ).
- 2.** Alliage de cuivre selon la revendication 1, dans lequel  
le contenu en B est compris entre 0,1 et 9,8 % en poids,  
le contenu en au moins un élément choisi dans le groupe Ni, Co, Al, Si, Fe, Zr et Mn est compris entre 0,5 et 40 %  
35 en poids de la quantité totale, et le rapport en volume total de l'élément B et du composé intermétallique de B avec  
au moins un élément choisi dans le groupe Cu, Ni, Co, Al, Si, Fe, Zr et Mn est compris entre 3,0 et 74,5 % en volume  
sur la base du volume total.
- 3.** Alliage de cuivre selon l'une quelconque des revendications 1 à 2, dans lequel l'alliage est fabriqué par un procédé  
40 de fonte.
- 4.** Alliage de cuivre selon l'une quelconque des revendications 1 à 2, dans lequel l'alliage est fabriqué par un procédé  
de frittage de poudre.
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- 50
- 55

**REFERENCES CITED IN THE DESCRIPTION**

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**Patent documents cited in the description**

- JP 2003124746 A [0002]
- JP HE1108166 B [0003]
- JP 08027531 A [0008]
- US 2809889 A [0008]
- US 4818307 A [0009]

**Non-patent literature cited in the description**

- Binary Alloy Phase Diagrams. vol. 1, 474-476 [0008]
- **Sauptel D.** Crystal growth of MgB<sub>2</sub> from Mg-Cu-B melt flux and superconducting properties. *Journal of Alloys and Compounds*, vol. 349 (1-2), 193-200 [0008]