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(54) **HIGH-STRENGTH COPPER ALLOY FORGING**

(57) The present invention pertains to a high-strength copper alloy forging which has excellent characteristics including high hardness, high strength and high thermal conductivity. This high-strength copper alloy forging contains, by mass, 3 to 7.2% of Ni, 0.7 to 1.8% of Si, 0.02 to 0.35% of Zr and 0.002 to 0.05% of P, and further contains, if necessary, one or more of Cr, Mn and Zn in a total amount of 1.5% or less. By virtue of the

actions of proper amounts of Zr and P, the high-strength copper alloy forging is less susceptible to cracking during working or heat treatment, and exhibits, after working and heat treatment, excellent characteristics including high hardness, high strength and high thermal conductivity, thus being suitable for use in injection molds for resins, aircraft components, and so on.

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Description**Technical Field**

5 **[0001]** The present invention relates to a high-strength copper alloy forging material suitable for forged moldings and the like, including resin injection mold materials.

Background Art

10 **[0002]** As alloys excellent in electrical conductivity and thermal conductivity, there have hitherto been used copper alloys such as brass (Cu-Zn-based), bronze (Cu-Sn-based), Be copper and Corson alloy (Cu-Ni-Si-based). In particular, Be copper, Corson alloy and the like have been used for resin injection mold materials, aircraft components and the like requiring strength and hardness, together with thermal conductivity. However, the above-described Be copper has concerns about toxicity of dust generated at the time of melting or working thereof, so that replacements therefor have
15 been demanded. Further, for the Corson alloy, higher thermal conductivity, higher strength and higher hardness have been demanded.

Furthermore, generally in the Cu alloys, cracks easily occur at the time of forging or heat treatment, so that there is also demanded improvement in ductility, in addition to hot workability.

20 **[0003]** As a measure for increasing strength and improving bending workability in foil bands of the copper alloys, there has recently been proposed copper alloys in which Mg, Sn, Ti, Zr, Al, Mn and the like are added to Cu-Ni-Si-based copper alloys (see PTLs 1 to 5). Mg and Sn dissolve in solid in a matrix to improve the strength. Ti, Zr, Al and Mn form compounds with sulfur, because of their strong affinity to sulfur, thereby decreasing segregation of sulfides to grain boundaries, which is responsible for hot-working cracks.

25 **[0004]** The copper alloy foil bands as shown in PTLs 2, 3 and 5 have a bending workability and a strength exceeding those of conventional copper alloy foil bands by adding Sn, Mn, Zr and the like and repeating hot rolling and cold rolling, or hot drawing and cold drawing, before and after solution treatment and aging treatment.

Citation List30 **Patent Literature****[0005]**

PTL 1: JP-A-2006-9108

35 PTL 2: JP-A-2008-196042

PTL 3: JP-A-2008-223136

40 PTL 4: JP-A-2008-266787

PTL 5: JP-A-2010-106363

Summary of Invention

45 **Technical Problem**

[0006] However, when Cu copper moldings are produced, working and forming are mainly performed by hot forging. Accordingly, in the case where rolling or drawing as performed in foil band production cannot be employed, even when
50 forged moldings are produced using compositions as shown in PTLs 2, 3 and 5, the high strength is not obtained.

In order to obtain the high strength, it is effective to increase the amounts of Ni and Si added. However, thermal conductivity or hot workability is deteriorated with an increase in the Ni or Si amount. Further, a crystallized material formed during coagulation or a precipitate formed during heat treatment increases to decrease ductility after the heat treatment.

55 **[0007]** The invention has been made against the background of the above circumstances, and an object thereof is to provide a high-strength copper alloy forging material which is usable for forged moldings and the like, including resin injection mold materials, and can provide properties of high hardness, high strength, high ductility and high thermal conductivity.

Solution to Problem

[0008] In order to solve the above-described problems, in the invention, an appropriate amount of Zr having an effect of suppressing precipitation of Ni_2Si on crystal grain boundaries to increase ductility is allowed to be contained in a Cu-Ni-Si-based alloy. Further, an appropriate amount of P which has an effect of increasing the density of fine precipitations and also forms a compound with Ni, Si and Zr, is allowed to be contained therein, which makes it possible to obtain a material having properties of high hardness, high strength, and high thermal conductivity.

[0009] According to a first aspect of the invention, there is provided a high-strength copper alloy forging material comprising, in mass%, 3 to 7.2% of Ni, 0.7 to 1.8% of Si, 0.02 to 0.35% of Zr and 0.002 to 0.05% of P.

[0010] According to a second aspect of the invention, there is provided a high-strength copper alloy forging material comprising, in mass%, 3 to 7.2% of Ni, 0.7 to 1.8% of Si, 0.02 to 0.35% of Zr and 0.002 to 0.05% of P, and further comprising 1.5% or less of one or two or more of Cr, Mn and Zn in total.

[0011] According to a third aspect of the invention, in the first or second aspect, the high-strength copper alloy forging material has a 0.2% yield strength of 650 MPa or more, an elongation of 5% or more and an electrical conductivity of 30% IACS or more.

Advantageous Effects of Invention

[0012] According to the invention, cracks are less likely to occur in a material during working and heat treatment, and there can be obtained the high-strength copper alloy forging material having properties of high hardness, high strength, and high thermal conductivity.

Description of Embodiments

[0013] Reasons for composition limitations of the respective components in the invention will be described below. Incidentally, all the contents of the following components are indicated by mass%. Further, "mass%" and "weight%" have the same meaning.

[0014] Ni: 3 to 7.2%

Si: 0.7 to 1.8%

Ni and Si form precipitate particles of an intermetallic compound which is mainly composed of fine Ni_2Si , by performing aging treatment, and significantly increase the strength of the alloy. Further, with precipitation of Ni_2Si in the aging treatment, electrical conductivity is improved, and thermal conductivity is improved. However, when the Ni concentration is less than 3% and the Si concentration is less than 0.7%, the desired strength is not obtained. Further, when the Ni concentration exceeds 7.2% and the Si concentration exceeds 1.8%, Ni_2Si , Ni_5Si_2 and the like are crystallized or precipitated in large amounts at the time of forging, resulting in easy occurrence of cracks at the time of forging or heat treatment. In addition, when the Ni concentration exceeds 7.2%, the electrical conductivity is also decreased, and the thermal conductivity is decreased. Considering the balance of the productivity and properties, the lower limit of the Ni concentration is preferably 3.5%, and the upper limit thereof is preferably 6.6%. The lower limit of the Si concentration is preferably 0.8%, and the upper limit thereof is preferably 1.7%. Incidentally, the Ni/Si ratio is preferably from 3.8 to 4.6. In the case of departing this ratio, excessive Ni or Si is dissolved in solid in a Cu matrix to decrease the thermal conductivity.

[0015] Zr: 0.02 to 0.35%

Zr forms a compound with sulfur, because of its strong affinity to sulfur, and decreases segregation of a sulfide to grain boundaries, which is responsible for working cracks (hot-working cracks), thereby improving workability (hot workability).

On the other hand, as a result of intensive research of the present inventors, it has been found that diffusion of Ni or Si is suppressed by containing Zr to decrease Ni_2Si precipitated on the grain boundaries, thereby improving ductility after the aging. In order to obtain this effect, Zr is allowed to be contained in an amount of 0.02% or more. However, when contained in an amount of more than 0.35%, productivity or the properties are deteriorated by increases and coagulation of crystallized materials such as Zr oxide and Ni_2SiZr . Accordingly, the upper limit thereof is 0.35%. Considering the balance of the productivity and the properties, the lower limit thereof is preferably 0.05%, and the upper limit thereof is preferably 0.3%.

[0016] P: 0.002 to 0.05%

P improves the strength by increasing the density of fine precipitates, and further forms a compound with Ni, Si and Zr, in which a slight amount of P is contained in Ni_2Si , Ni_2SiZr or the like, thereby increasing the hardness. In order to obtain these effects, P is allowed to be contained in an amount of 0.002% or more. However, when contained in an amount of more than 0.05%, the thermal conductivity is largely decreased. Accordingly, the upper limit thereof is 0.05%. For the same reason, the lower limit thereof is preferably 0.01%, and the upper limit thereof is preferably 0.04%.

[0017] Cr, Mn and Zn: 1.5% or less in total

At least one of Cr, Mn and Zn is allowed to be contained as desired.

Cr forms an intermetallic compound with Si, and has effects of improving the strength and miniaturizing crystal grains. Mn forms a compound with sulfur, because of its strong affinity to sulfur, and decreases segregation of a sulfide to grain boundaries, which is responsible for working cracks (hot-working cracks), thereby improving workability (hot workability).

Zn improves the strength by solid-solution hardening. Further, when it is possible to use inexpensive brass scrap at the time of dissolution, the production cost can be reduced. However, when Cr, Mn and Zn are excessively contained in the total amount, the thermal conductivity is decreased. It is therefore preferred that the total amount of Cr, Mn and Zn is 1.5% or less.

More preferably, the total amount of Cr, Mn and Zn is 1.0% or less. Further, when at least one of Cr, Mn and Zn is allowed to be contained, the total amount thereof is preferably 0.1 % or more.

[0018] The high-strength copper alloy forging material of the invention has the above-described metal composition, and the balance is composed of Cu and unavoidable impurities.

[0019] The high-strength copper alloy forging material of the invention can be produced by an ordinary method.

The copper alloy used in the invention can be ingoted by an ordinary method. For example, it is possible to melt a material under a vacuum atmosphere, an inert atmosphere, an atmospheric atmosphere or the like to obtain an ingot. The atmosphere is preferably the vacuum atmosphere or the inert atmosphere. However, the copper alloy can also be ingoted, for example, in an atmospheric high-frequency furnace. Further, secondary melting using an electroslog remelting furnace or the like may be performed. It is also possible to obtain a plate material by a continuous forging method.

[0020] The copper alloy is subjected to working as needed. The contents of the working are not particularly limited in the invention, and even when any working method is used, it is possible to obtain the properties of the invention. Incidentally, considering the productivity, the working is preferably hot working, and further preferably hot working performed at 600°C or more. However, it is also possible to obtain the properties similar to those of the hot working even by working at room temperature. Further, the working may be a combination of the hot working and cold working. Furthermore, as the working, forging is preferred, and hot forging is more preferred. It is still more preferred that the hot forging is performed at 600°C or more. As a forging method, there can be employed a known method such as pressing, hammering or rolling.

[0021] It is also possible that the copper alloy material worked is subjected to solution treatment after or during the working. Conditions of the solution treatment include, for example, maintaining at 800 to 1,000°C for 1 to 10 hours, and thereafter cooling at a cooling rate of 5°C/sec or more in a temperature range of 500°C or more, in order to sufficiently dissolve Ni and Si in solid.

The copper alloy material worked can be subjected to aging treatment after the solution treatment or after the working. Conditions of the aging treatment include, for example, maintaining at 400 to 500°C for 1 to 30 hours.

The resulting high-strength copper alloy material has properties such as a 0.2% yield strength of 650 MPa or more, an elongation of 5% or more, and an electrical conductivity of 30% IACS or more.

[0022] Incidentally, the high-strength copper alloy forging material of the invention has excellent properties as a forging material. However, in the composition of the invention, even a casting material not subjected to the above-described working such as the forging can provide properties such as good ductility.

Examples

[0023] Examples of the invention will be described below.

Raw materials were blended so as to give component compositions (including other unavoidable impurities) of Table 1, and melted in a vacuum induction melting furnace to prepare alloys of 100 mm (diameter)×200 mm (length). These alloys were subjected to hot forging using a hammer at 900°C to form plate materials having a thickness of 25 mm. After maintaining at 970°C for 4 hours, solution treatment by water cooling was performed. Thereafter, aging treatment suitable for materials of the respective compositions was performed at 400 to 500°C for 1 to 30 hours to obtain sample materials.

[0024]

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[Table 1]

Sample Material No		Component (% by mass)										Aging Conditions (°C × hr)
		Cu	Ni	Si	Zr	P	Cr	Mn	Zn	Total of Cr, Mn and Zn	Ni/Si Ratio	
Example	1	Balance	4.16	0.95	0.09	0.018	-	-	-	-	4.38	475°C × 3 hr
	2	Balance	5.15	1.14	0.16	0.017					4.52	475°C × 3 hr
	3	Balance	4.83	1.12	0.08	0.004	0.43	0.19	0.33	0.95	4.31	450°C × 10 hr
	4	Balance	7.20	1.80	0.22	0.034	-	-	-	-	4.00	450°C × 10 hr
	5	Balance	3.70	0.92	0.27	0.048	0.02	-	-	0.02	4.02	475°C × 3 hr
	6	Balance	4.10	0.98	0.09	0.016	0.02	0.40	-	0.42	4.18	475°C × 3 hr
	7	Balance	3.10	0.74	0.03	0.020	-	-	-	-	4.19	475°C × 3 hr
	8	Balance	5.04	1.17	0.32	0.049	-	0.20	0.50	0.70	4.31	450°C × 10 hr
	9	Balance	6.60	1.65	0.12	0.003	0.40	-	-	0.40	4.00	450°C × 10 hr
Comparative Example	10	Balance	7.30	1.57	-	-	-	-	-	-	4.65	425°C × 30 hr
	11	Balance	4.24	0.99	-	-	-	-	-	-	4.28	450°C × 1 hr
	12	Balance	8.37	0.93	-	-	-	-	-	-	9.00	475°C × 3 hr
	13	Balance	3.77	0.95	0.16	-	-	-	-	-	3.97	475°C × 3 hr
	14	Balance	4.25	0.93	-	0.055	-	-	-	-	4.57	500°C × 1 hr
	15	Balance	4.85	1.18	0.36	0.023	0.49	0.50	0.58	1.57	4.11	450°C × 10 hr
	16	Balance	7.77	1.87	0.10	0.022	0.42	-	-	0.42	4.16	450°C × 10 hr
	17	Balance	2.20	0.55	0.01	0.002	-	-	-	-	4.00	450°C × 1 hr
	18	Balance	8.12	2.05	0.12	0.030	-	-	-	-	3.96	450°C × 10 hr
	19	Balance	5.33	1.39	0.08	0.006	3.03	0.22	0.15	3.40	3.83	450°C × 10 hr

[0025] As to the sample materials prepared, evaluations shown below were performed.

(Tensile Test)

[0026] An ordinary-temperature tensile test was performed on the respective sample materials based on JIS Z2201 (2010) and JIS Z2241 (2010) to evaluate the 0.2% yield strength (Y. S.), the tensile strength (T. S.), the elongation and the reduction of area. The measurement results are shown in Table 2.

(Vickers Hardness)

[0027] For the respective sample materials, the Vickers hardness was measured at a load of 5 kg based on JIS Z2244 (2010). The measurement results are shown in Table 2.

(Thermal Conductivity)

[0028] For the respective sample materials, the electrical conductivity was measured. As shown in the Wiedemann-Franz law, the thermal conductivity has an approximately proportional relationship to the electrical conductivity, so that the thermal conductivity can be evaluated by the electrical conductivity. The measurement results are shown in Table 2.

[0029]

[Table 2]

Sample Material No		0.2% Y. S (MPa)	T. S. (MPa)	Elongation (%)	Reduction of Area (%)	Vickers Hardness (Hv)	Electrical Conductivity (%IACS)
Example	1	667	772	8.8	19.0	266	36.1
	2	728	809	7.2	20.8	291	35.1
	3	750	806	13.2	19.5	296	35.0
	4	676	781	6.6	16.0	315	30.2
	5	733	789	11.0	22.0	288	31.0
	6	699	766	8.1	16.2	264	36.1
	7	689	755	6.5	13.0	268	40.0
	8	781	866	5.9	18.1	321	33.4
	9	651	766	10.0	16.3	292	33.1
Comparative Example	10	513	607	2.4	5.9	277	31.2
	11	610	620	1.8	5.9	253	37.7
	12	623	764	4.6	10.5	264	29.6
	13	616	717	7.6	15.4	255	35.2
	14	735	813	1.8	5.2	301	33.2
	15	762	830	4.1	13.6	302	29.2
	16	740	855	3.6	11.0	322	28.5
	17	460	520	6.9	16.2	203	52.5
	18	760	856	2.5	8.3	333	23.2
	19	712	811	3.0	9.2	297	29.0

[0030] As shown in Table 2, the sample materials of Examples of the invention had a 0.2% yield strength of 650 MPa or more, an elongation of 5% or more and an electrical conductivity of 30% IACS or more, and further had a hardness equivalent to or more than that of the sample materials of Comparative Examples

As described above, according to the invention, it has been revealed that the excellent properties of increasing the strength, the ductility and the hardness while maintaining the high electrical conductivity, namely the high thermal conductivity, are obtained by containing appropriate amounts of Zr and P in the Ni-Si-Cu alloy

[0031] The invention has been described in detail with reference to specific embodiments thereof. However, it will be apparent to those skilled in the art that various changes and modifications may be made without departing from the spirit and scope of the invention. This application is based on Japanese Patent Application No. 2011-030660 filed on Feb. 16, 2011, the contents of which are incorporated herein by reference.

Industrial Applicability

[0032] According to the high-strength copper alloy forging material of the invention, appropriate amounts of Zr and P act to cause cracks to be less likely to occur in the material at the time of working or heat treatment. After the working and the heat treatment, the forging material of the invention can have the properties of high hardness, high strength and high thermal conductivity, and can be suitably used for resin injection mold materials, aircraft components and the like.

Claims

1. A high-strength copper alloy forging material comprising, in mass%, 3 to 7.2% of Ni, 0.7 to 1.8% of Si, 0.02 to 0.35% of Zr and 0.002 to 0.05% of P.
2. A high-strength copper alloy forging material comprising, in mass%, 3 to 7.2% of Ni, 0.7 to 1.8% of Si, 0.02 to 0.35% of Zr and 0.002 to 0.05% of P, and further comprising 1.5% or less of one or two or more of Cr, Mn and Zn in total.
3. The high-strength copper alloy forging material according to claim 1 or 2, having a 0.2% yield strength of 650 MPa or more, an elongation of 5% or more and an electrical conductivity of 30% IACS or more.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/053414

A. CLASSIFICATION OF SUBJECT MATTER C22C9/06(2006.01)i, B21J1/00(2006.01)i, C22F1/08(2006.01)i, C22F1/00(2006.01)n According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C22C9/06, B21J1/00, C22F1/08, C22F1/00 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2012 Kokai Jitsuyo Shinan Koho 1971-2012 Toroku Jitsuyo Shinan Koho 1994-2012 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 4630387 B1 (The Furukawa Electric Co., Ltd.), 09 February 2011 (09.02.2011), claims; paragraph [0028]; table 1 (Family: none)	1, 2
X	JP 2010-106363 A (The Furukawa Electric Co., Ltd.), 13 May 2010 (13.05.2010), claims; paragraph [0031]; tables 1, 2 (Family: none)	1, 2
X	JP 2006-283059 A (Kobe Steel, Ltd.), 19 October 2006 (19.10.2006), claims; paragraph [0031]; tables 1 to 3 (Family: none)	1-3
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: “A” document defining the general state of the art which is not considered to be of particular relevance “E” earlier application or patent but published on or after the international filing date “L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) “O” document referring to an oral disclosure, use, exhibition or other means “P” document published prior to the international filing date but later than the priority date claimed		“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention “X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone “Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art “&” document member of the same patent family
Date of the actual completion of the international search 18 April, 2012 (18.04.12)		Date of mailing of the international search report 01 May, 2012 (01.05.12)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 4-218631 A (Nippon Mining Co., Ltd.), 10 August 1992 (10.08.1992), claims; paragraph [0012]; table 1 (Family: none)	1-3

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

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- JP 2011030660 A [0031]