to the molten solder at the timing when the chip is placed on the molten solder, it does not inhibit the convection of the molten solder.

[0019] Therefore, the solder alloy containing Ge makes it possible not only to suppress Ni leaching, but also to discharge voids generated at the bonded interface to the outside. Then, in the Sn-Ag-Cu-Ni-Co-Ge solder alloy, in order to suppress Ni leaching and generation of voids at a higher level, it is necessary to mix Co, Ni, and Ge in a well-balanced manner.

[0020] Furthermore, because Ag_3Sn is precipitated at the grain boundaries by adding Ag and the strength of the solder alloy is improved, it is necessary to consider the balance of Ag content.

[0021] The present inventors have studied in detail the overall balance of Co and Ni content ratio, Ge content, and Ag content in Sn-Ag-Cu-Ni-Co-Ge solder alloy. As a result, it was found that such a solder alloy exhibits high tensile strength and suppresses Ni leaching and void generation, and present invention was completed based on this finding.

[0022] Furthermore, it was also found that the optimum mechanical properties for the form of the solder balls used for BGA can be obtained by intentionally adding an appropriate amount of Bi, which was conventionally considered to embrittle the solder alloy by solidification segregation. In addition to this, it was also found that the solder alloy can be suitably used as a solder ball in view of further suppressing Ni leaching and having capability of sufficient use for fine Cu electrodes with Ni plating because Bi distorts not only the crystal structure of $(Cu,Ni)_6Sn_5$ but also the Sn matrix in the solder alloy by dissolving in Sn and coexists with Ge.

[0023] The present inventions obtained from these finding are as follows.

(1) A lead-free and antimony-free solder alloy having an alloy composition consisting of, by mass%, Ag: 1.0 to 4.0%, Cu: 0.1 to 1.0%, Ni: 0.005 to 0.3%, Co: 0.003 to 0.1%, and Ge: 0.001 to 0.015% with the balance being Sn,

wherein the alloy composition satisfies the following relation (1):

$$0.00030 < (Ni/Co) \times (1/Ag) \times Ge < 0.05 \qquad (1)$$

wherein Ni, Co, Ag, and Ge in the relation (1) each represent the contents (mass%) in the alloy composition.

(1a) In one aspect, there is provided a lead-free and antimony-free solder alloy having an alloy composition consisting of, by mass%, Ag: 1.0 to 4.0%, Cu: 0.1 to 1.0%, Ni: 0.005 to 0.3%, Co: 0.003 to 0.1%, Ge: 0.001 to 0.015%, and optionally one or more selected from the group consisting of Mn, Pd, Au, Pt, Cr, V, Mo, and Nb each with an upper limit of 0.01% by

mass%, with the balance being Sn, wherein the alloy composition satisfies the following relation (1):

$$0.00030 < (Ni/Co) \times (1/Ag) \times Ge < 0.05 \qquad (1)$$

wherein Ni, Co, Ag, and Ge in the relation (1) each represent the contents (mass%) in the alloy composition.

[0024] (2) A lead-free and antimony-free solder alloy having an alloy composition consisting of, by mass%, Ag: 1.0 to 4.0%, Cu: 0.1 to 1.0%, Ni: 0.005 to 0.3%, Co: 0.005 to 0.1%, Ge: 0.001 to 0.015%, and Bi: 0.1 to 9.0% with the balance being Sn,

wherein the alloy composition satisfies the following relation (1):

$$0.00030 < (Ni/Co) \times (1/Ag) \times Ge < 0.05 \qquad (1)$$

wherein Ni, Co, Ag, and Ge in the relation (1) each represent the contents (mass%) in the alloy composition.

(2a) In another aspect, there is provided a lead-free and antimony-free solder alloy having an alloy composition consisting of, by mass%, Ag: 1.0 to 4.0%, Cu: 0.1 to 1.0%, Ni: 0.005 to 0.3%, Co: 0.005 to 0.1%, Ge: 0.001 to 0.015%, Bi: 0.1 to 9.0%, and optionally Fe with an upper limit of 0.01% by mass%, and optionally one or more selected from the group consisting of Mn, Pd, Au, Pt, Cr, V, Mo, and Nb each with an upper limit of 0.01% by mass%, with the balance being Sn, wherein the alloy composition satisfies the following relation (1):

$$0.00030 < (Ni/Co) \times (1/Ag) \times Ge < 0.05 \qquad (1)$$

wherein Ni, Co, Ag, and Ge in the relation (1) each represent the contents (mass%) in the alloy composition

[0025] (3) The lead-free and antimony-free solder alloy according to (2) above, wherein the Bi content is 1.0 to 5.0%.

(4) The lead-free and antimony-free solder alloy according to (2) above, wherein the Bi content is 2.0 to 4.0%.

(5) The lead-free and antimony-free solder alloy according to any one of (1) to (4) above, wherein the alloy composition further comprises one or more selected from the group consisting of Mn, Pd, Au, Pt, Cr, V, Mo, and Nb each with an upper limit of 0.01% by mass%.

(6) The lead-free and antimony-free solder alloy according to any one of (1) to (5) above, wherein the Ag content is 1.5 to 3.5%.

(7) The lead-free and antimony-free solder alloy according to any one of (1) to (5) above, wherein the Ag content is 2.0 to 3.0%.

[0026] (8) The lead-free and antimony-free solder alloy according to any one of (1) to (7) above, wherein ΔT, which is defined as a difference between a liquidus temperature and a solidus temperature, is 250°C or less.

[0027] (9) The lead-free and antimony-free solder alloy according to any one of (1) to (7) above, wherein ΔT, which is defined as a difference between a liquidus temperature and a solidus temperature, is 120°C or less.

[0028] (10) The lead-free and antimony-free solder alloy according to any one of (1) to (7) above, wherein ΔT, which is defined as a difference between a liquidus temperature and a solidus temperature, is 100°C or less.

(11) The lead-free and antimony-free solder alloy according to any one of (1) to (10) above,

wherein the alloy composition satisfies the following relation (2):

$$0.00150 \leq (Ni/Co) \times (1/Ag) \times Ge \leq 0.00833 \qquad (2)$$

wherein Ni, Co, Ag, and Ge in the relation (2) each represent the contents (mass%) in the alloy composition.

[0029] (12) A solder ball comprising the lead-free and antimony-free solder alloy according to any one of (1) to (11) above.

(13) The solder ball according to (12) above, having an average particle diameter of 1 to 1000 μm.

(14) The solder ball according to (12) or (13) above, having a sphericity of 0.95 or more.

(15) The solder ball according to (12) or (13) above, having a sphericity of 0.99 or more.

(16) A ball grid array formed using the solder ball according to any one of (12) to (15) above.

(16a) Use of the solder ball described herein for forming a ball grid array.

(17) A solder joint comprising the lead-free and antimony-free solder alloy according to any one of (1) to (11) above.

(18) The lead-free and antimony-free solder alloy according to any one of (2) to (4) above, wherein the alloy composition further comprises Fe with an upper limit of 0.01% by mass%.

(19) The lead-free and antimony-free solder alloy according to (18) above, wherein the Ag content is 1.5 to 3.5%.

(20) The lead-free and antimony-free solder alloy according to (18) above, wherein the Ag content is 2.0 to 3.0%.

(21) The lead-free and antimony-free solder alloy according to any one of (18) to (20) above, wherein ΔT, which is defined as a difference between a liquidus temperature and a solidus temperature, is 250°C or less.

(22) The lead-free and antimony-free solder alloy according to any one of (18) to (20) above, wherein ΔT, which is defined as a difference between a liquidus temperature and a solidus temperature, is 120°C or less.

(23) The lead-free and antimony-free solder alloy according to any one of (18) to (20) above, wherein ΔT, which is defined as a difference between a liquidus temperature and a solidus temperature, is 100°C or less.

(24) The lead-free and antimony-free solder alloy according to any one of (18) to (23) above,

wherein the alloy composition satisfies the following relation (2):

[0058] 5. Other

A bonding method using a solder alloy according to the present invention may be performed according to an ordinary method e.g. using a reflow method. The heating temperature may be appropriately adjusted depending on a heat resistance of the chip or the liquidus temperature of the solder alloy. About 240°C is preferable as the heating temperature from the viewpoint of suppressing thermal damage to the chip. A melting temperature of the solder alloy for performing flow soldering may be approximately 20°C higher than the liquidus temperature. In a case where bonding is conducted by using the solder alloy according to the present invention, the structure can be further made minuteness by considering a cooling rate during solidification. For example, the solder joint is cooled at a cooling rate of 2 to 3°C/s or higher. Other bonding conditions can be appropriately adjusted depending on the alloy composition of the solder alloy.

[0059] The solder alloy according to the present invention enables a low α-ray alloy to be produced by using a low α-ray material as a raw material therefor. When such a low α-ray-alloy is used for forming solder bumps in the periphery of a memory, soft errors can be suppressed.

Examples

[0060] For the solder alloys constituted from alloy compositions as shown in Tables 1 to 9, ΔT obtained from the liquidus line temperature and the solidus line temperature, Ni leaching, and the presence or absence of voids were evaluated as follows. The tensile strength was also evaluated.

[0061] (1) ΔT (°C~~K~~)

Each solder alloy as shown in Tables 1 to 9 was prepared, and the melting temperature of the solder was measured. The measurement of the solidus temperature was performed according to JIS Z3198-1. The liquidus temperature was measured, instead of JIS Z3198-1, with a method with DSC which is similar to the measurement method for a solidus temperature according to JIS Z3198-1. ΔT (°C~~K~~), which is the difference between the measured liquidus temperature and solidus temperature, was determined. When ΔT (°C~~K~~) was less than 100°C~~K~~, it was rated as “S”, when it was 100 to 120°C~~K~~, it was rated as “A”, when it was over 120°C~~K~~ and 250°C~~K~~ or less, it was rated as “B” and when it was over 250°C~~K~~, it was rated as “D”.

[0062] (2) Ni leaching

A preform with a thickness of 250 μm and made of alloy composition as shown in Tables 1 to 9 was mounted on a Cu lead frame. Thereafter, an IC chip having a back metal on

[0065]

Table 1

	Alloy Composition (mass%)						Relation (1)	ΔT (°C~~K~~)	Ni leaching	void
	Sn	Ag	Cu	Ni	Co	Ge				
Ex. 1	Bal.	3.0	0.4	0.01	0.01	0.005	0.00167	S	B	B
Ex. 2	Bal.	3.0	0.4	0.03	0.01	0.005	0.00500	S	B	B
Ex. 3	Bal.	3.0	0.5	0.04	0.01	0.005	0.00667	S	B	B
Ex. 4	Bal.	2.4	0.4	0.05	0.01	0.005	0.01042	S	B	B
Ex. 5	Bal.	3.0	0.4	0.06	0.01	0.005	0.01000	S	B	B
Ex. 6	Bal.	3.0	0.5	0.08	0.01	0.005	0.01333	S	B	B
Ex. 7	Bal.	3.0	0.5	0.01	0.04	0.005	0.00042	S	B	B
Ex. 8	Bal.	3.0	0.5	0.02	0.04	0.005	0.00083	S	B	B
Ex. 9	Bal.	3.0	0.4	0.03	0.02	0.005	0.00250	S	B	B
Ex. 10	Bal.	3.0	0.5	0.03	0.02	0.003	0.00150	S	B	B
Ex. 11	Bal.	3.0	0.5	0.04	0.01	0.003	0.00400	S	B	B
Ex. 12	Bal.	3.0	0.5	0.05	0.01	0.003	0.00500	S	B	B
Ex. 13	Bal.	3.0	0.5	0.04	0.02	0.005	0.00333	S	B	B
Ex. 14	Bal.	3.0	0.4	0.05	0.02	0.005	0.00417	S	B	B
Ex. 15	Bal.	3.0	0.5	0.07	0.03	0.005	0.00389	S	B	B
Ex. 16	Bal.	2.8	0.5	0.07	0.03	0.005	0.00417	S	B	B
Ex. 17	Bal.	3.0	0.4	0.03	0.08	0.005	0.00063	S	B	B
Ex. 18	Bal.	3.0	0.4	0.04	0.09	0.005	0.00074	S	B	B
Ex. 19	Bal.	3.0	0.5	0.05	0.05	0.005	0.00167	A	B	B
Ex. 20	Bal.	3.0	0.7	0.03	0.01	0.005	0.00500	S	B	B
Ex. 21	Bal.	3.0	0.7	0.05	0.01	0.005	0.00833	S	B	B
Ex. 22	Bal.	3.0	0.7	0.09	0.01	0.005	0.01500	S	B	B
Ex. 23	Bal.	3.0	0.7	0.03	0.03	0.005	0.00167	S	B	B
Ex. 24	Bal.	3.0	0.7	0.05	0.04	0.005	0.00208	S	B	B
Ex. 25	Bal.	3.0	0.7	0.07	0.03	0.005	0.00389	S	B	B
Ex. 26	Bal.	1.0	0.7	0.07	0.03	0.005	0.01167	S	B	B
Ex. 27	Bal.	3.0	0.1	0.07	0.03	0.005	0.00389	A	B	B

Table 1-continued

	Alloy Composition (mass%)						Relation (1)	ΔT (°C~~K~~)	Ni leaching	void
	Sn	Ag	Cu	Ni	Co	Ge				
Ex. 28	Bal.	4.0	0.5	0.07	0.03	0.005	0.00292	A	B	B
Ex. 29	Bal.	3.0	0.5	0.05	0.005	0.005	0.01667	S	B	B
Ex. 30	Bal.	3.0	0.4	0.01	0.01	0.015	0.00500	S	B	B
Ex. 31	Bal.	3.0	1.0	0.04	0.01	0.003	0.00400	S	B	B
Comp. Ex. 1	Bal.	1.0	0.5	0.05	0.01	0.015	0.07500	S	B	D
Comp. Ex. 2	Bal.	3.0	0.5	0.005	0.01	0.001	0.00017	S	D	B
Comp. Ex. 3	Bal.	3.0	0.5	0.05	0.2	0.003	0.00025	D	-	-
Comp. Ex. 4	Bal.	0.1	0.5	0.01	0.02	0.003	0.01500	S	B	B
Comp. Ex. 5	Bal.	5.0	0.5	0.03	0.02	0.003	0.00090	S	B	B
Comp. Ex. 6	Bal.	3.0	0.5	0.001	0.02	0.015	0.00025	S	D	B
Comp. Ex. 7	Bal.	3.0	0.5	1.0	0.1	0.003	0.01000	D	-	-

Ex = Example

Comp. Ex. = Comparative Example

The underline indicates that it does not fall within the scope of the present invention.

[0066]

Table 2

	Alloy Composition (mass%)							Relation (1)	ΔT (°C~~K~~)	Ni leaching	void
	Sn	Ag	Cu	Ni	Co	Ge	Bi				
Ex. 32	Bal.	3.0	0.4	0.01	0.01	0.005	0.1	0.00167	S	B	B
Ex. 33	Bal.	3.0	0.4	0.03	0.01	0.005	0.1	0.00500	S	B	B
Ex. 34	Bal.	3.0	0.5	0.04	0.01	0.005	0.1	0.00667	S	B	B
Ex. 35	Bal.	3.0	0.4	0.05	0.01	0.005	0.1	0.00833	S	B	B
Ex. 36	Bal.	3.0	0.5	0.08	0.01	0.005	0.1	0.01333	S	B	B
Ex. 37	Bal.	3.0	0.5	0.01	0.04	0.005	0.1	0.00042	S	B	B
Ex. 38	Bal.	3.0	0.4	0.03	0.02	0.005	0.1	0.00250	S	B	B
Ex. 39	Bal.	3.0	0.5	0.03	0.02	0.003	0.1	0.00150	S	B	B
Ex. 40	Bal.	3.0	0.5	0.05	0.01	0.003	0.1	0.00500	S	B	B

Table 2-continued

	Alloy Composition (mass%)							Relation (1)	ΔT (°C~~K~~)	Ni leaching	void
	Sn	Ag	Cu	Ni	Co	Ge	Bi				
Ex. 41	Bal.	3.0	0.5	0.04	0.02	0.005	0.1	0.00333	S	B	B
Ex. 42	Bal.	3.0	0.4	0.05	0.02	0.005	0.1	0.00417	S	B	B
Ex. 43	Bal.	3.0	0.5	0.07	0.03	0.005	0.1	0.00389	S	B	B
Ex. 44	Bal.	3.0	0.4	0.04	0.09	0.005	0.1	0.00074	S	B	B
Ex. 45	Bal.	3.0	0.5	0.05	0.05	0.005	0.1	0.00167	A	B	B
Ex. 46	Bal.	3.0	0.7	0.03	0.01	0.005	0.1	0.00500	S	B	B
Ex. 47	Bal.	3.0	0.7	0.09	0.01	0.005	0.1	0.01500	S	B	B
Ex. 48	Bal.	3.0	0.7	0.03	0.03	0.005	0.1	0.00167	S	B	B
Ex. 49	Bal.	3.0	0.7	0.05	0.04	0.005	0.1	0.00208	S	B	B
Ex. 50	Bal.	3.0	0.7	0.07	0.03	0.005	0.1	0.00389	S	B	B
Ex. 51	Bal.	1.0	0.7	0.07	0.03	0.005	0.1	0.01167	A	B	B
Ex. 52	Bal.	3.0	0.1	0.07	0.03	0.005	0.1	0.00389	A	B	B
Ex. 53	Bal.	4.0	0.5	0.07	0.03	0.005	0.1	0.00292	A	B	B
Ex. 54	Bal.	3.0	0.5	0.05	0.005	0.005	0.1	0.01667	S	B	B
Ex. 55	Bal.	3.0	0.4	0.01	0.01	0.015	0.1	0.00500	S	B	B
Ex. 56	Bal.	3.0	1.0	0.04	0.01	0.003	0.1	0.00400	S	B	B
Comp. Ex. 8	Bal.	1.0	0.5	0.05	0.01	0.015	0.1	0.07500	S	B	D
Comp. Ex. 9	Bal.	3.0	0.5	0.005	0.01	0.001	0.1	0.00017	S	D	B
Comp. Ex. 10	Bal.	3.0	0.5	0.05	0.2	0.003	0.1	0.00025	D	-	-
Comp. Ex. 11	Bal.	0.1	0.5	0.01	0.02	0.003	0.1	0.01500	S	B	B
Comp. Ex. 12	Bal.	5.0	0.5	0.03	0.02	0.003	0.1	0.00090	S	B	B
Comp. Ex. 13	Bal.	3.0	0.5	0.001	0.02	0.015	0.1	0.00025	S	D	B
Comp. Ex. 14	Bal.	3.0	0.5	1.0	0.1	0.003	0.1	0.01000	D	-	-

Ex = Example

Comp. Ex. = Comparative Example

The underline indicates that it does not fall within the scope of the present invention.

[0067]

Table 3

	Alloy Composition (mass%)							Relation (1)	ΔT (°C~~K~~)	Ni leaching	void
	Sn	Ag	Cu	Ni	Co	Ge	Bi				
Ex. 57	Bal.	3.0	0.4	0.01	0.01	0.005	0.5	0.00167	S	B	B
Ex. 58	Bal.	3.0	0.5	0.04	0.01	0.005	0.5	0.00667	S	B	B
Ex. 59	Bal.	3.0	0.4	0.06	0.01	0.005	0.5	0.01000	S	B	B
Ex. 60	Bal.	3.0	0.5	0.01	0.04	0.005	0.5	0.00042	S	B	B
Ex. 61	Bal.	3.0	0.4	0.03	0.02	0.005	0.5	0.00250	S	B	B
Ex. 62	Bal.	3.0	0.5	0.04	0.01	0.003	0.5	0.00400	S	B	B
Ex. 63	Bal.	3.0	0.5	0.04	0.02	0.005	0.5	0.00333	S	B	B
Ex. 64	Bal.	3.0	0.5	0.07	0.03	0.005	0.5	0.00389	S	B	B
Ex. 65	Bal.	3.0	0.4	0.03	0.08	0.005	0.5	0.00063	S	B	B
Ex. 66	Bal.	3.0	0.5	0.05	0.05	0.005	0.5	0.00167	A	B	B
Ex. 67	Bal.	3.0	0.7	0.05	0.01	0.005	0.5	0.00833	S	B	B
Ex. 68	Bal.	3.0	0.7	0.03	0.03	0.005	0.5	0.00167	S	B	B
Ex. 69	Bal.	3.0	0.7	0.07	0.03	0.005	0.5	0.00389	S	B	B
Ex. 70	Bal.	3.0	0.1	0.07	0.03	0.005	0.5	0.00389	A	B	B
Ex. 71	Bal.	3.0	0.5	0.05	0.005	0.005	0.5	0.01667	S	B	B
Ex. 72	Bal.	3.0	1.0	0.04	0.01	0.003	0.5	0.00400	S	B	B

Ex = Example

Comp. Ex. = Comparative Example

The underline indicates that it does not fall within the scope of the present invention.

[0068]

Table 4

	Alloy Composition (mass%)							Relation (1)	ΔT (°C~~K~~)	Ni leaching	void
	Sn	Ag	Cu	Ni	Co	Ge	Bi				
Ex. 73	Bal.	3.0	0.4	0.03	0.01	0.005	1.0	0.00500	S	B	B
Ex. 74	Bal.	3.0	0.4	0.05	0.01	0.005	1.0	0.00833	S	B	B
Ex. 75	Bal.	3.0	0.5	0.08	0.01	0.005	1.0	0.01333	S	B	B
Ex. 76	Bal.	3.0	0.5	0.02	0.04	0.005	1.0	0.00083	S	B	B
Ex. 77	Bal.	3.0	0.5	0.03	0.02	0.003	1.0	0.00150	S	B	B
Ex. 78	Bal.	3.0	0.5	0.05	0.01	0.003	1.0	0.00500	S	B	B
Ex. 79	Bal.	3.0	0.4	0.05	0.02	0.005	1.0	0.00417	S	B	B
Ex. 80	Bal.	3.0	0.5	0.07	0.03	0.005	1.0	0.00389	S	B	B
Ex. 81	Bal.	3.0	0.4	0.04	0.09	0.005	1.0	0.00074	S	B	B
Ex. 82	Bal.	3.0	0.7	0.03	0.01	0.005	1.0	0.00500	S	B	B
Ex. 83	Bal.	3.0	0.7	0.09	0.01	0.005	1.0	0.01500	S	B	B
Ex. 84	Bal.	3.0	0.7	0.05	0.04	0.006	1.0	0.00250	S	B	B
Ex. 85	Bal.	1.0	0.7	0.07	0.03	0.005	1.0	0.01167	A	B	B
Ex. 86	Bal.	4.0	0.5	0.07	0.03	0.005	1.0	0.00292	A	B	B
Ex. 87	Bal.	3.0	0.4	0.01	0.01	0.015	1.0	0.00500	S	B	B

Ex = Example

Comp. Ex. = Comparative Example

The underline indicates that it does not fall within the scope of the present invention.

[0069]

Table 5

	Alloy Composition (mass%)							Relation (1)	ΔT (°C~~K~~)	Ni leaching	void
	Sn	Ag	Cu	Ni	Co	Ge	Bi				
Ex. 88	Bal.	3.0	0.4	0.01	0.01	0.005	2.0	0.00167	S	B	B
Ex. 89	Bal.	3.0	0.4	0.03	0.01	0.005	2.0	0.00500	S	B	B
Ex. 90	Bal.	3.0	0.4	0.05	0.01	0.005	2.0	0.00833	S	B	B
Ex. 91	Bal.	3.0	0.4	0.06	0.01	0.005	2.0	0.01000	S	B	B
Ex. 92	Bal.	2.5	0.8	0.08	0.008	0.008	2.0	0.03200	S	B	B
Ex. 93	Bal.	3.0	0.5	0.01	0.04	0.005	2.0	0.00042	S	B	B
Ex. 94	Bal.	3.0	0.5	0.02	0.04	0.005	2.0	0.00083	S	B	B
Ex. 95	Bal.	3.0	0.5	0.03	0.02	0.003	2.0	0.00150	S	B	B
Ex. 96	Bal.	3.0	0.5	0.04	0.01	0.003	2.0	0.00400	S	B	B
Ex. 97	Bal.	3.0	0.5	0.04	0.02	0.005	2.0	0.00333	S	B	B
Ex. 98	Bal.	3.0	0.4	0.05	0.02	0.005	2.0	0.00417	S	B	B
Ex. 99	Bal.	3.0	0.5	0.07	0.03	0.005	2.0	0.00389	S	B	B
Ex. 100	Bal.	3.0	0.4	0.03	0.08	0.005	2.0	0.00063	S	B	B
Ex. 101	Bal.	3.0	0.5	0.05	0.05	0.005	2.0	0.00167	B	B	B
Ex. 102	Bal.	3.0	0.7	0.03	0.01	0.005	2.0	0.00500	S	B	B
Ex. 103	Bal.	3.0	0.7	0.09	0.01	0.005	2.0	0.01500	S	B	B
Ex. 104	Bal.	3.0	0.7	0.03	0.03	0.005	2.0	0.00167	S	B	B
Ex. 105	Bal.	3.0	0.7	0.07	0.03	0.005	2.0	0.00389	A	B	B
Ex. 106	Bal.	1.0	0.7	0.07	0.03	0.005	2.0	0.01167	A	B	B
Ex. 107	Bal.	4.0	0.5	0.07	0.03	0.005	2.0	0.00292	A	B	B
Ex. 108	Bal.	3.0	0.5	0.05	0.005	0.005	2.0	0.01667	S	B	B
Ex. 109	Bal.	3.0	1.0	0.04	0.01	0.003	2.0	0.00400	S	B	B
Comp. Ex. 15	Bal.	1.0	0.5	0.05	0.01	0.015	2.0	0.07500	S	B	D
Comp. Ex. 16	Bal.	3.0	0.5	0.005	0.01	0.001	2.0	0.00017	S	D	B

Ex = Example

Comp. Ex. = Comparative Example

The underline indicates that it does not fall within the scope of the present invention.

[0070]

Table 6

	Alloy Composition (mass%)							Relation (1)	ΔT (°C~~K~~)	Ni leaching	void
	Sn	Ag	Cu	Ni	Co	Ge	Bi				
Ex. 110	Bal.	3.0	0.4	0.01	0.01	0.005	3.0	0.00167	S	B	B
Ex. 111	Bal.	3.0	0.4	0.03	0.01	0.005	3.0	0.00500	S	B	B
Ex. 112	Bal.	3.0	0.5	0.04	0.01	0.005	3.0	0.00667	S	B	B
Ex. 113	Bal.	3.0	0.4	0.06	0.01	0.005	3.0	0.01000	S	B	B
Ex. 114	Bal.	3.0	0.5	0.08	0.01	0.005	3.0	0.01333	S	B	B
Ex. 115	Bal.	3.0	0.5	0.01	0.04	0.005	3.0	0.00042	S	B	B
Ex. 116	Bal.	3.0	0.4	0.03	0.02	0.005	3.0	0.00250	S	B	B
Ex. 117	Bal.	3.0	0.5	0.03	0.02	0.003	3.0	0.00150	S	B	B
Ex. 118	Bal.	3.0	0.5	0.04	0.01	0.003	3.0	0.00400	S	B	B
Ex. 119	Bal.	3.0	0.5	0.04	0.02	0.005	3.0	0.00333	S	B	B
Ex. 120	Bal.	3.0	0.4	0.05	0.02	0.005	3.0	0.00417	S	B	B
Ex. 121	Bal.	3.0	0.5	0.07	0.03	0.005	3.0	0.00389	S	B	B
Ex. 122	Bal.	3.0	0.4	0.03	0.08	0.005	3.0	0.00063	S	B	B
Ex. 123	Bal.	3.0	0.4	0.04	0.09	0.005	3.0	0.00074	S	B	B
Ex. 124	Bal.	3.0	0.5	0.05	0.05	0.005	3.0	0.00167	B	B	B
Ex. 125	Bal.	3.0	0.7	0.05	0.01	0.005	3.0	0.00833	S	B	B
Ex. 126	Bal.	2.5	0.7	0.09	0.01	0.005	3.0	0.01800	S	B	B
Ex. 127	Bal.	3.0	0.7	0.03	0.03	0.005	3.0	0.00167	S	B	B
Ex. 128	Bal.	3.0	0.7	0.07	0.03	0.005	3.0	0.00389	A	B	B
Ex. 129	Bal.	1.0	0.7	0.07	0.03	0.005	3.0	0.01167	A	B	B
Ex. 130	Bal.	3.0	0.1	0.07	0.03	0.005	3.0	0.00389	B	B	B
Ex. 131	Bal.	3.0	0.5	0.05	0.005	0.005	3.0	0.01667	S	B	B
Ex. 132	Bal.	3.0	0.4	0.01	0.01	0.015	3.0	0.00500	S	B	B
Ex. 133	Bal.	3.0	1.0	0.04	0.01	0.003	3.0	0.00400	S	B	B
Comp. Ex. 17	Bal.	1.0	0.5	0.05	0.01	0.015	3.0	0.07500	S	B	D
Comp. Ex. 18	Bal.	3.0	0.5	0.005	0.01	0.001	3.0	0.00017	S	D	B

Ex = Example

Comp. Ex. = Comparative Example

The underline indicates that it does not fall within the scope of the present invention.

[0071]

Table 7

	Alloy Composition (mass%)								Relation (1)	ΔT (°C ~~K~~)	Ni leaching	void
	Sn	Ag	Cu	Ni	Co	Ge	Bi	optional element				
Ex. 134	Bal.	3.0	0.4	0.01	0.01	0.005	4.0		0.00167	S	B	B
Ex. 135	Bal.	2.0	0.4	0.03	0.01	0.005	4.0		0.00750	S	B	B
Ex. 136	Bal.	3.0	0.5	0.04	0.01	0.005	4.0		0.00667	S	B	B
Ex. 137	Bal.	3.0	0.4	0.05	0.01	0.005	4.0		0.00833	S	B	B
Ex. 138	Bal.	3.0	0.5	0.08	0.01	0.005	4.0		0.01333	S	B	B
Ex. 139	Bal.	3.0	0.5	0.01	0.04	0.005	4.0		0.00042	S	B	B
Ex. 140	Bal.	3.0	0.5	0.02	0.04	0.005	4.0		0.00083	S	B	B
Ex. 141	Bal.	3.0	0.4	0.03	0.02	0.005	4.0		0.00250	S	B	B
Ex. 142	Bal.	3.0	0.5	0.04	0.01	0.003	4.0		0.00400	S	B	B
Ex. 143	Bal.	3.0	0.5	0.05	0.01	0.003	4.0		0.00500	S	B	B
Ex. 144	Bal.	3.0	0.5	0.04	0.02	0.005	4.0		0.00333	S	B	B
Ex. 145	Bal.	3.0	0.4	0.05	0.02	0.005	4.0		0.00417	S	B	B
Ex. 146	Bal.	3.0	0.5	0.07	0.03	0.005	4.0		0.00389	S	B	B
Ex. 147	Bal.	3.0	0.4	0.03	0.08	0.005	4.0		0.00063	S	B	B
Ex. 148	Bal.	3.0	0.4	0.04	0.09	0.005	4.0		0.00074	S	B	B
Ex. 149	Bal.	3.0	0.5	0.05	0.05	0.005	4.0		0.00167	B	B	B
Ex. 150	Bal.	3.0	0.7	0.05	0.01	0.005	4.0		0.00833	S	B	B
Ex. 151	Bal.	3.0	0.7	0.09	0.01	0.005	4.0		0.01500	S	B	B
Ex. 152	Bal.	3.0	0.8	0.03	0.03	0.005	4.0		0.00167	S	B	B
Ex. 153	Bal.	3.0	0.7	0.05	0.04	0.005	4.0		0.00208	S	B	B
Ex. 154	Bal.	1.0	0.7	0.07	0.03	0.005	4.0		0.01167	B	B	B
Ex. 155	Bal.	3.0	0.1	0.07	0.03	0.005	4.0		0.00389	B	B	B
Ex. 156	Bal.	4.0	0.5	0.07	0.03	0.005	4.0		0.00292	B	B	B
Ex. 157	Bal.	3.0	0.5	0.05	0.005	0.005	4.0		0.01667	S	B	B
Ex. 158	Bal.	3.0	1.0	0.04	0.01	0.003	4.0		0.00400	S	B	B
Ex. 159	Bal.	3.0	0.4	0.01	0.01	0.005	2.0	Mn: 0.01	0.00167	S	B	B

Table 7-continued

	Alloy Composition (mass%)								Relation (1)	ΔT (°C ~~K~~)	Ni leaching	void
	Sn	Ag	Cu	Ni	Co	Ge	Bi	optional element				
Ex. 160	Bal.	3.0	0.4	0.01	0.01	0.005	2.0	Pd: 0.01	0.00167	S	B	B
Ex. 161	Bal.	3.0	0.4	0.01	0.01	0.005	2.0	Au: 0.01	0.00167	S	B	B
Ex. 162	Bal.	3.0	0.4	0.01	0.01	0.005	2.0	Cr: 0.01	0.00167	S	B	B
Ex. 163	Bal.	3.0	0.4	0.01	0.01	0.005	2.0	Fe: 0.01	0.00167	S	B	B
Ex. 164	Bal.	3.0	0.4	0.01	0.01	0.005	2.0	V: 0.01	0.00167	S	B	B
Ex. 165	Bal.	3.0	0.4	0.01	0.01	0.005	2.0	Mo: 0.01	0.00167	S	B	B
Ex. 166	Bal.	3.0	0.4	0.01	0.01	0.005	2.0	Nb: 0.01	0.00167	S	B	B
Comp. Ex. 19	Bal.	1.0	0.5	0.05	0.01	0.015	4.0		0.07500	S	B	D
Comp. Ex. 20	Bal.	3.0	0.5	0.005	0.01	0.001	4.0		0.00017	S	D	B

Ex = Example

Comp. Ex. = Comparative Example

The underline indicates that it does not fall within the scope of the present invention.

[0072]

Table 8

	Alloy Composition (mass%)							Relation (1)	ΔT (°C~~K~~)	Ni leaching	void
	Sn	Ag	Cu	Ni	Co	Ge	Bi				
Ex. 167	Bal.	3.0	0.4	0.03	0.01	0.005	6.0	0.00500	S	B	B
Ex. 168	Bal.	3.0	0.4	0.05	0.01	0.005	6.0	0.00833	S	B	B
Ex. 169	Bal.	3.0	0.5	0.08	0.01	0.005	6.0	0.01333	S	B	B
Ex. 170	Bal.	3.0	0.5	0.02	0.04	0.005	6.0	0.00083	S	B	B
Ex. 171	Bal.	3.0	0.5	0.03	0.02	0.003	6.0	0.00150	S	B	B
Ex. 172	Bal.	3.0	0.5	0.05	0.01	0.003	6.0	0.00500	S	B	B
Ex. 173	Bal.	3.0	0.4	0.05	0.02	0.005	6.0	0.00417	S	B	B
Ex. 174	Bal.	3.0	0.5	0.07	0.03	0.005	6.0	0.00389	S	B	B
Ex. 175	Bal.	3.0	0.4	0.04	0.09	0.005	6.0	0.00074	S	B	B
Ex. 176	Bal.	3.0	0.7	0.03	0.01	0.005	6.0	0.00500	S	B	B
Ex. 177	Bal.	3.0	0.7	0.09	0.01	0.005	6.0	0.01500	A	B	B
Ex. 178	Bal.	3.0	0.7	0.05	0.04	0.005	6.0	0.00208	S	B	B
Ex. 179	Bal.	1.0	0.7	0.07	0.03	0.005	6.0	0.01167	B	B	B
Ex. 180	Bal.	4.0	0.5	0.07	0.03	0.005	6.0	0.00292	B	B	B
Ex. 181	Bal.	3.0	0.4	0.01	0.01	0.015	6.0	0.00500	S	B	B

Ex = Example

Comp. Ex. = Comparative Example

The underline indicates that it does not fall within the scope of the present invention.

[0073]

Table 9

	Alloy Composition (mass%)							Relation (1)	ΔT (°C~~K~~)	Ni leaching	void
	Sn	Ag	Cu	Ni	Co	Ge	Bi				
Ex. 182	Bal.	3.0	0.4	0.01	0.01	0.005	9.0	0.00167	S	B	B
Ex. 183	Bal.	3.0	0.4	0.03	0.01	0.005	9.0	0.00500	S	B	B
Ex. 184	Bal.	3.0	0.5	0.04	0.01	0.005	9.0	0.00667	S	B	B
Ex. 185	Bal.	3.0	0.4	0.05	0.01	0.005	9.0	0.00833	S	B	B
Ex. 186	Bal.	3.0	0.5	0.08	0.01	0.005	9.0	0.01333	S	B	B
Ex. 187	Bal.	3.0	0.5	0.01	0.04	0.005	9.0	0.00042	S	B	B
Ex. 188	Bal.	3.0	0.4	0.03	0.02	0.005	9.0	0.00250	S	B	B
Ex. 189	Bal.	3.0	0.5	0.03	0.02	0.003	9.0	0.00150	S	B	B
Ex. 190	Bal.	3.0	0.5	0.05	0.01	0.003	9.0	0.00500	S	B	B
Ex. 191	Bal.	3.0	0.5	0.04	0.02	0.005	9.0	0.00333	S	B	B
Ex. 192	Bal.	3.0	0.4	0.05	0.02	0.005	9.0	0.00417	S	B	B
Ex. 193	Bal.	3.0	0.5	0.07	0.03	0.005	9.0	0.00389	S	B	B
Ex. 194	Bal.	3.0	0.4	0.04	0.09	0.005	9.0	0.00074	A	B	B
Ex. 195	Bal.	3.0	0.7	0.03	0.01	0.005	9.0	0.00500	S	B	B
Ex. 196	Bal.	3.0	0.7	0.2	0.01	0.0025	9.0	0.01667	S	B	B
Ex. 197	Bal.	3.0	0.7	0.03	0.03	0.005	9.0	0.00167	S	B	B
Ex. 198	Bal.	3.0	0.7	0.05	0.04	0.005	9.0	0.00208	A	B	B
Ex. 199	Bal.	3.0	0.7	0.07	0.03	0.005	9.0	0.00389	B	B	B
Ex. 200	Bal.	3.0	0.7	0.3	0.04	0.003	9.0	0.00750	B	B	B
Ex. 201	Bal.	3.0	0.1	0.07	0.03	0.005	9.0	0.00389	B	B	B
Ex. 202	Bal.	4.0	0.5	0.07	0.03	0.005	9.0	0.00292	B	B	B
Ex. 203	Bal.	3.0	1.0	0.04	0.01	0.003	9.0	0.00400	A	B	B

Table 9-continued

	Alloy Composition (mass%)							Relation (1)	ΔT (°C~~K~~)	Ni leaching	void
	Sn	Ag	Cu	Ni	Co	Ge	Bi				
Comp. Ex. 21	Bal.	1.0	0.5	0.05	0.01	0.015	9.0	0.07500	S	B	D
Comp. Ex. 22	Bal.	3.0	0.5	0.005	0.01	0.001	9.0	0.00017	S	D	B
Comp. Ex. 23	Bal.	3.0	0.5	0.05	0.2	0.003	9.0	0.00025	D	-	-
Comp. Ex. 24	Bal.	0.1	0.5	0.01	0.02	0.003	9.0	0.01500	S	B	B
Comp. Ex. 25	Bal.	5.0	0.5	0.03	0.02	0.003	9.0	0.00090	S	B	B
Comp. Ex. 26	Bal.	3.0	0.5	0.001	0.02	0.015	9.0	0.00025	S	D	B
Comp. Ex. 27	Bal.	3.0	0.5	1.0	0.1	0.003	9.0	0.01000	D	-	-

Ex = Example

Comp. Ex. = Comparative Example

The underline indicates that it does not fall within the scope of the present invention.

[0074] As shown in Tables 1 to 9, according to Examples 1 to 203, the content of each constituent element and the relation (1) were satisfied for all the alloy compositions, whereby Ni leaching and voids at bonded interfaces were not observed. In addition, it was also confirmed that they exhibited higher tensile strength than Comparative Examples 1 to 27.

[0075] On the other hand, according to Comparative Examples 1, 8, 15, 17, 19, and 21, the contents of Ag, Co, Ge, and Ni were not well-balanced due to exceeding the upper limit of the relation (1), so that voids were generated. According to Comparative Examples 2, 9, 16, 18, 20, 22, and 27, the balance of the contents of Ag, Co, Ge, and Ni was poor because the relation (1) is lower than the lower limit, so that they were inferior with regard to Ni leaching.

[0076] The evaluation regarding ΔT of Comparative Examples 3, 10, and 23 were “D” because the liquidus temperature was high due to high Co content. Because the liquidus temperature was 500°C or higher and a solder joint could not be formed, no other evaluation was performed. For Comparative Examples 4, 11, and 24, it was confirmed that since a small amount of Ag_3Sn was precipitated due to low Ag-content, the tensile strength was low as compared with those of Examples 1 to 203. For Comparative Examples 5, 12, and 25, it was confirmed that since coarse Ag_3Sn was precipitated due to too high Ag content, the tensile strength was low as compared with those of Examples 1 to 203.

[0077] For Comparative Examples 6, 13, and 26, Ni leaching could not be suppressed because the Ni content was small. Comparative Examples 7, 14, and 27 were not evaluated

CLAIMS

1. A lead-free and antimony-free solder alloy having an alloy composition consisting of, by mass%, Ag: 1.0 to 4.0%, Cu: 0.1 to 1.0%, Ni: 0.005 to 0.3%, Co: 0.003 to 0.1%, ~~and~~ Ge: 0.001 to 0.015%, and

optionally one or more selected from the group consisting of Mn, Pd, Au, Pt, Cr, V, Mo, and Nb each with an upper limit of 0.01% by mass%, with the balance being Sn,

wherein the alloy composition satisfies the following relation (1):

$$0.00030 < (Ni/Co) \times (1/Ag) \times Ge < 0.05 \qquad (1)$$

wherein Ni, Co, Ag, and Ge in the relation (1) each represent the contents (mass%) in the alloy composition.

2. A lead-free and antimony-free solder alloy having an alloy composition consisting of, by mass%, Ag: 1.0 to 4.0%, Cu: 0.1 to 1.0%, Ni: 0.005 to 0.3%, Co: 0.005 to 0.1%, Ge: 0.001 to 0.015%, ~~and~~ Bi: 0.1 to 9.0%, and

optionally Fe with an upper limit of 0.01% by mass%, and

optionally one or more selected from the group consisting of Mn, Pd, Au, Pt, Cr, V, Mo, and Nb each with an upper limit of 0.01% by mass%, with the balance being Sn,

wherein the alloy composition satisfies the following relation (1):

$$0.00030 < (Ni/Co) \times (1/Ag) \times Ge < 0.05 \qquad (1)$$

wherein Ni, Co, Ag, and Ge in the relation (1) each represent the contents (mass%) in the alloy composition.

3. The lead-free and antimony-free solder alloy according to claim 1, wherein the alloy composition consists of, by mass%, Ag: 1.0 to 4.0%, Cu: 0.1 to 1.0%, Ni: 0.005 to 0.3%, Co: 0.003 to 0.1%, and Ge: 0.001 to 0.015% with the balance being Sn.

4. The lead-free and antimony-free solder alloy according to claim 2, wherein the alloy composition consists of, by mass%, Ag: 1.0 to 4.0%, Cu: 0.1 to 1.0%, Ni: 0.005 to 0.3%, Co: 0.005 to 0.1%, Ge: 0.001 to 0.015%, and Bi: 0.1 to 9.0% with the balance being Sn.

5. The lead-free and antimony-free solder alloy according to claim 2, wherein the alloy composition consists of, by mass%, Ag: 1.0 to 4.0%, Cu: 0.1 to 1.0%, Ni: 0.005 to 0.3%, Co: 0.005 to 0.1%, Ge: 0.001 to 0.015%, Bi: 0.1 to 9.0%, and Fe with an upper limit of 0.01% by mass% with the balance being Sn.

~~3~~6. The lead-free and antimony-free solder alloy according to any one of claims 2, 4 and 5, wherein the Bi content is 1.0 to 5.0%.

~~4~~7. The lead-free and antimony-free solder alloy according to any one of claims 2, 4 and 5, wherein the Bi content is 2.0 to 4.0%.

~~5. The lead-free and antimony-free solder alloy according to any one of claims 1 to 4, wherein the alloy composition further comprises one or more selected from the group consisting of Mn, Pd, Au, Pt, Cr, V, Mo, and Nb each with an upper limit of 0.01% by mass%.~~

~~6~~8. The lead-free and antimony-free solder alloy according to any one of claims 1 to ~~5~~7, wherein the Ag content is 1.5 to 3.5%.

~~7~~9. The lead-free and antimony-free solder alloy according to any one of claims 1 to ~~5~~7, wherein the Ag content is 2.0 to 3.0%.

~~8~~10. The lead-free and antimony-free solder alloy according to any one of claims 1 to ~~7~~9, wherein ΔT, which is defined as a difference between a liquidus temperature and a solidus temperature, is 250°C or less.

~~9~~11. The lead-free and antimony-free solder alloy according to any one of claims 1 to ~~7~~9, wherein ΔT, which is defined as a difference between a liquidus temperature and a solidus temperature, is 120°C or less.

~~10~~12. The lead-free and antimony-free solder alloy according to any one of claims 1 to ~~7~~9, wherein ΔT, which is defined as a difference between a liquidus temperature and a solidus temperature, is 100°C or less.

~~11~~13. The lead-free and antimony-free solder alloy according to any one of claims 1 to ~~10~~12, wherein the alloy composition satisfies the following relation (2):

$$0.00150 \leq (Ni/Co) \times (1/Ag) \times Ge \leq 0.00833 \quad (2)$$

wherein Ni, Co, Ag, and Ge in the relation (2) each represent the contents (mass%) in the alloy composition.

~~12~~14. A solder ball comprising the lead-free and antimony-free solder alloy according to any one of claims 1 to ~~11~~13.

~~13~~15. The solder ball according to claim ~~12~~14, having an average particle diameter of 1 to 1000 μm.

~~14~~16. The solder ball according to claim ~~12~~ 14 or ~~13~~15, having a sphericity of 0.95 or more.

~~15~~17. The solder ball according to claim ~~12~~ 14 or ~~13~~15, having a sphericity of 0.99 or more.

~~16~~18. ~~A ball grid array formed using~~ Use of the solder ball according to any one of claims ~~12~~ 14 to ~~15~~17 for forming a ball grid array.

~~17~~19. A solder joint comprising the lead-free and antimony-free solder alloy according to any one of claims 1 to ~~11~~13.

~~18. The lead-free and antimony-free solder alloy according to any one of claims 2 to 4, wherein the alloy composition further comprises Fe with an upper limit of 0.01% by mass%.~~

~~19. The lead-free and antimony-free solder alloy according to claim 18, wherein the Ag content is 1.5 to 3.5%.~~

~~20. The lead-free and antimony-free solder alloy according to claim 18, wherein the Ag content is 2.0 to 3.0%.~~

~~21. The lead-free and antimony-free solder alloy according to any one of claims 18 to 20,~~

wherein ΔT, which is defined as a difference between a liquidus temperature and a solidus temperature, is 250°C or less.

22. The lead-free and antimony-free solder alloy according to any one of claims 18 to 20, wherein ΔT, which is defined as a difference between a liquidus temperature and a solidus temperature, is 120°C or less.

23. The lead-free and antimony-free solder alloy according to any one of claims 18 to 20, wherein ΔT, which is defined as a difference between a liquidus temperature and a solidus temperature, is 100°C or less.

24. The lead-free and antimony-free solder alloy according to any one of claims 18 to 23, wherein the alloy composition satisfies the following relation (2):

$$0.00150 \leq (Ni/Co) \times (1/Ag) \times Ge \leq 0.00833 \quad (2)$$

wherein Ni, Co, Ag, and Ge in the relation (2) each represent the contents (mass%) in the alloy composition.

25. A solder ball comprising the lead-free and antimony-free solder alloy according to any one of claims 18 to 24.

26. The solder ball according to claim 25, having an average particle diameter of 1 to 1000 μm.

27. The solder ball according to claim 25 or 26, having a sphericity of 0.95 or more.

28. The solder ball according to claim 25 or 26, having a sphericity of 0.99 or more.

29. A ball grid array formed using the solder ball according to any one of claims 25 to 28.

30. A solder joint comprising the lead-free and antimony-free solder alloy according to any one of claims 18 to 24.