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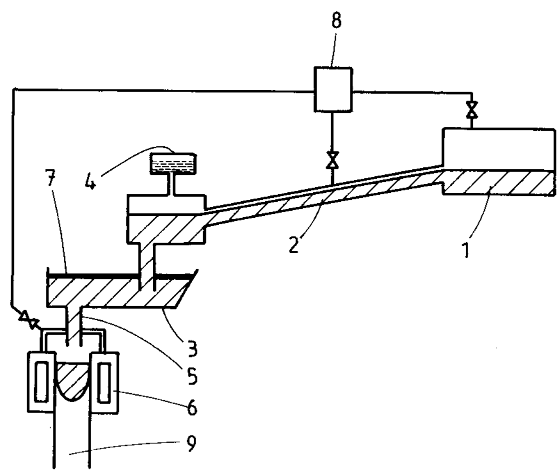
(54) High vacuum apparatus member and vacuum apparatus

(57) A material suitable for vacuum apparatuses which is easily dehydrogenated by baking. The material has a composition of high-purity oxygen-free copper with a purity of 99.99 wt% or greater, which contains prior to baking 1 to 15 ppm of Zr and 3 ppm or less of oxygen.



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The invention relates to a material or to members to be used for the manufacture of high-vacuum appartuses such as power transmitter tubes, external anodes which also serve as vacuum containers for microwave tubes, vacuum deposition and sputtering apparatuses, klystrons, waveguides, acceleration cavity containers for accelerators, etc., from which hydrogen is easily removed by baking, as well as to a vacuum apparatus comprising such material or members.

Conventionally, materials or members for the manufacture of high-vacuum apparatuses have generally been made of high-purity oxygen-free copper which satisfies required excellent electrical conductivity and thermal conductivity and includes low residual gas for preventing reduction in the degreee of vacuum in a vacuum apparatus due to residual gas in the material from which the apparatus is made. Such low-residual-gas including high-purity oxygen-free copper is manufactured by degassing of normal oxygen-free copper in a reducing or vacuum atmosphere, or by addition of phophorus for deoxygenation. High-purity oxygen-free copper produced in this manner contains 3 ppm or less of oxygen and 0.2 to 0.5 ppm of hydrogen, and vacuum apparatuses made of such high-purity oxygen-fee copper are subjected to dehydrogenatoina by vacuum annealing, called "baking", before use to guard against reduction in the degree of vacuum in a vacuum apparatus due to an out-gas from the material of the apparatus in a high vacuum.

However, even with dehydrogenation by baking prior to use of vacuum apparatuses manufactured using the aforementioned high-purity oxygen-free copper, certain problems result, since hydrogen contained in the high-purity oxygen-free copper is trapped by residual oxygen because of its strong affinity thereto, thus rendering the dehydrogenation more difficult. Consequently, when vacuum apparatuses manufactured using high-purity oxygen-free copper containing such oxygen-trapped hydrogen are used in a high vacuum, the residual hydrogen is gradually released and causes a reduction in the degree of vacuum.

The object of the present invention is to provide a high-purity copper alloy material suitable for high vacuum apparatuses which has after baking a reduced residual hydrogen content.

This object is solved in accordance with the present invention by a high-purity copper material having the features of claim 1. Preferred applications of such material are subject matter of claims 3 to 5.

The inventors have conducted research aimed at producing a material suitable as vacuum apparatus member made of a copper alloy from which hydrogen is easily removed by baking, conventionally high-purity oxygen-free copper, which does not lead to a reduced degree of vacuum due to out-gassing hydrogen when used in a high vacuum, as well as a vacuum apparatus comprising such a vacuum apparatus member, and have found that a copper alloy prepared by adding 1 to 15 ppm of zirconium (Zr) to normal high-purity oxygen-free copper allows easy removal of hydrogen by baking and has a very low level of out-gassing of residual hydrogen from the material in a high vacuum, thus preventing reduction in the degree of vacuum.

The present invention has been accomplished on the basis of this finding, and is characterized by being a material having a composition of high-purity oxygen-free copper with a purity of 99.99 wt% or greater, which contains 1 to 15 ppm of Zr and 3 ppm or less of oxygen; and vacuum apparatuses constructed with the aforementioned material having a composition of high-purity copper with a purity of 99.99 wt% or greater, which contains 1 to 15 ppm of Zr and 3 ppm or less of oxygen.

The material of the present invention allows easy removal of hydrogen by baking when it contains 1 to 15 ppm of Zr because, since Zr is an element with a very strong affinity for oxygen, residual trace oxygen in the copper alloy combines preferentially with Zr and is not dissociated therefrom even by heating during baking. Therefor, the residual trace oxygen in the high-purity copper alloy does not trap hydrogen, and thus the hydrogen is easily removed during baking.

However, a Zr content of less than 1 ppm is not preferred since this is insufficient for combining with the residual oxygen in the copper alloy, and conversely a Zr content of more than 15 ppm is not preferred since this reduces the hydrogen-removing effect during baking. The range of the Zr content is therefore established to be 1 to 15 ppm. A more preferred range of the Zr content is 3 to 10 ppm.

Since up to 3 ppm of oxygen in the copper alloy may combine with Zr in the above-mentioned range of 1 to 15 ppm, the oxygen content of the vacuum apparatus member of the present invention is preferably up to 3 ppm.

To manufacture vacuum apparatus members containing 1 to 15 ppm of Zr and 3 ppm or less of oxygen according to the present invention, first, electrolytic copper with a purity of 99.99 wt% or greater is melted in a melting furnace under constant protection with CO + N_2 gas, and the resulting molten metal is poured into a ladle while Zr is added to the flow of the molten metal for adjustement of the components to a prescribed composition.

The vacuum apparatus material of the present invention and a method of prodcuing it will now be explained in further detail by way of the following example and the attached drawings which is a schematic view of an apparatus for producing the vacuum apparatus material according to the present invention.

The apparatus shown in the drawings comprises a melting furnace 1, a spout 2, a tundish 3, an addition apparatus 4, a nozzle 5, a mold 6, a covering 7 of graphite particles and a sealing gas source 8 in order to produce an ingot 9.

First, electrolytic copper with a purity of 99.99 wt% or greater was prepared and melted in the melting furnace 1 in a CO + N_2 atmosphere. The resulting molten metal was passed through the spout 2 sealed with CO + N_2 gas and transported to the tundish 3, and Zr was added from the addition apparatus 4 to the flowing molten metal before it reached the tundish 3. The surface of the molten metal in the tundish 3 was covered with a layer of graphite particles 7 to prevent its oxidation. The molten metal was then fed from the tundish 3 via the nozzle 5 to the mold 6 which was also sealed with CO + N_2 gas, and an ingot 9 was obtained.

Table 1 below shows the composition of the ingot obtained in this manner as detrmined by measurement of the Zr and oxygen contents. Specimens of 25 mm length, 25 mm width and 8 mm thickness were cut out from the ingot, and further lathed to prepare vacuum apparatus members of the present invention (1 to 10 of Table 1), vacuum apparatus members for comparison (1 to 3 of Table 1) and vacuum apparatus members of the conventional art (1 to 3 of Table 1), each having a diameter of 20 mm and a thickness of 4 mm.

The vacuum apparatus material or members of the present invention 1 to 10, vacuum apparatus members for comparison 1 to 3 and vacuum apparatus members of the conventional art 1 to 3 were subjected to baking for one hour at a temperature of 500 °C in a vacuum atmosphere of 266 x 10^{-5} Pa (2 x 10^{-5} Torr) and these baked vacuum apparatus members of the present invention, vacuum apparatus members for comparison and vacuum apparatus members of the conventional art were further charged into an out-gas measuring apparatus to measure the out-gassing rate of hydrogen gas in a high-vacuum atmosphere of 133 x 10^{-10} Pa (1 x 10^{-10} Torr) while at a temperature of 500 °C. The results are given in Table 1.

TABLE 1

Vacuum apparatus member		Composition				Out-gassing rate (Torr• 1/sec.• cm^2)
		Electrolytic copper purity (%)	Zr (ppm)	Oxygen (ppm)	P (ppm)	
Present invention	1	99.998	3	1.8	-	1.33×10^{-11}
	2	99.998	4	2.0	-	2.17×10^{-11}
	3	99.998	3	1.7	-	2.34×10^{-11}
	4	99.998	1	0.7	-	6.75×10^{-12}
	5	99.998	7	1.8	-	8.98×10^{-12}
	6	99.998	12	2.0	-	1.10×10^{-11}
	7	99.998	14	2.7	-	2.14×10^{-11}
	8	99.998	6	1.2	-	9.77×10^{-12}
	9	99.998	11	1.5	-	7.29×10^{-12}
	10	99.998	10	2.0	-	1.01×10^{-11}
Comparison	1	99.998	7	5.0 *	-	6.21×10^{-10}
	2	99.998	0.6 *	1.8	-	2.70×10^{-10}
	3	99.998	18 *	1.2	-	8.29×10^{-11}
Conventional Art	1	99.998	-	2.0	3.1	1.26×10^{-10}
	2	99.998	-	1.5	2.8	8.92×10^{-11}
	3	99.998	-	2.5	-	1.94×10^{-10}
(Values marked with * are outside the range of the invention)						

The results shown in Table 1 demonstrate that the vacuum apparatus members of the present invention which contained 1 to 15 ppm of Zr and 3 ppm or less of oxygen all had lower values for the out-gassing rate of hydrogen gas in comparison with the vacuum apparatus members of the conventional art which did not contain Zr, and hence the hydrogen gas was more easily removed during the baking. In contrast, it was shown that the removal of hydrogen gas during baking was somewhat difficult in the case of the vacuum apparatus members for comparison 1-2 which were outside the ranges of 1 to 15 ppm of Zr and 3 ppm or less of oxygen. Also, as observed in the case of the vacuum apparatus member for comparison 3, a Zr content exceeding 15 ppm is not preferred as this causes more difficult removal of hydrogen gas during baking.

As explained above, a material for vacuum apparatus members according to the present invention offers easier removal of hydrogen during baking than vacuum apparatus members of the ceonventional art, and therefore it produces the excellent industrial effect of allowing the production of vacuum apparatuses with superior performance.

Claims

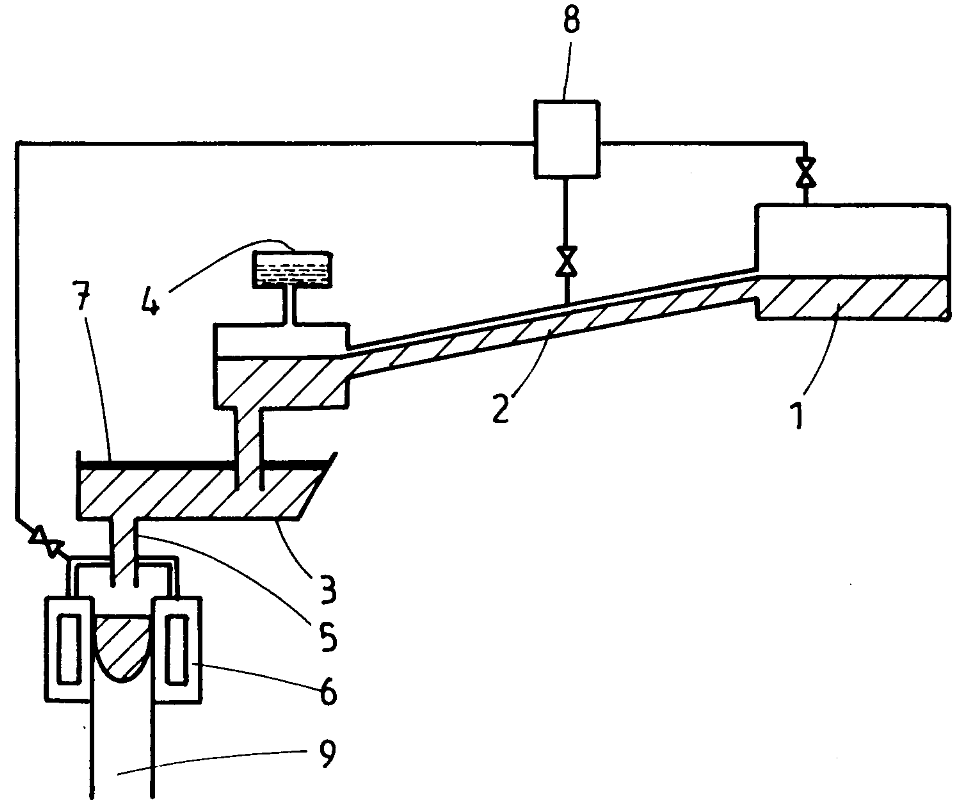
1. High vacuum apparatus member comprising of high-purity copper material, having a purity of 99.99 wt% or higher and containing prior to annealing (baking) hydrogen and 3 ppm or less of oxygen,
characterized in that
the material contains for easy dehydrogention by annealing (baking) 1 to 15 ppm Zr.

2. Material of claim 1, characterized in that it contains 3 to 10 ppm Zr.

3. Use of he high-purity copper material of claim 1 or 2 for constructing high vacuum apparatuses.

4. Use of the high-purity copper material of claim 1 or 2 for constructing external anodes, which also serve as vacuum container, suitable for microwave tubes, etc.

5. Use of the high-purity copper material of claim 1 or 2 for constructing acceleration cavity containers for accelerators.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EUROPEAN SEARCH REPORT

Application Number
EP 95 10 7446

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US-A-5 077 005 (NIPPON MINING CO.) 31 December 1991 *Tables and claims* ---	1-5	C22C9/00
X	US-A-4 717 436 (MITSUBISHI K.K.) 5 January 1988 *Tables and claims* ---	1-5	
X	EP-A-0 296 596 (FURUKAWA ELECTRIC CO.) 28 December 1988 *Page 3, Tables 1 and 3 and claims* ---	1-5	
X	PATENT ABSTRACTS OF JAPAN vol. 13 no. 156 (C-585) ,14 April 1989 & JP-A-63 312934 (HITACHI CABLE LTD) 21 December 1988, *Sample 2 in Table of patent document* * abstract * ---	1-5	
X	PATENT ABSTRACTS OF JAPAN vol. 12 no. 122 (C-488) ,15 April 1988 & JP-A-62 243727 (HITACHI CABLE LTD) 24 October 1987, *Sample 6 in Table of patent document* * abstract * ---	1-5	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C22C
Y	JOURNAL OF METALS, vol. 45, no. 3, March 1993 pages 68-70, RAJAINMAKI,H., KOLEHMAINEN,M.,HELENIUS,A. 'The Production and Application of Oxygen-Free Copper' *Page 70, middle column* --- -/--	1,3-5	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	5 October 1995	Badcock, G

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X : particularly relevant if taken alone
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Y	METALL, vol. 44, no. 11, November 1990 pages 1067-1070, HELENIUS,A.,KOLEHMAINEN,M., RAJAINMAKI,H. 'Current and Future Uses of Oxygen-Free Copper' *Page 1069 and p.1070, right hand column* ---	1,3-5	
A	PATENT ABSTRACTS OF JAPAN vol. 12 no. 70 (C-479) ,4 March 1988 & JP-A-62 207834 (NIPPON MINING CO. LTD.) 12 September 1987, *Example in patent document* * abstract * -----	1-5	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)

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