(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 135 964 A2

(12) # EUROPEAN PATENT APPLICATION

(43) Date of publication:
23.12.2009 Bulletin 2009/52

(51) Int Cl.:
C22C 9/04 *(2006.01)*

(21) Application number: **09008100.1**

(22) Date of filing: **19.06.2009**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK TR

(30) Priority: **20.06.2008 JP 2008161635**

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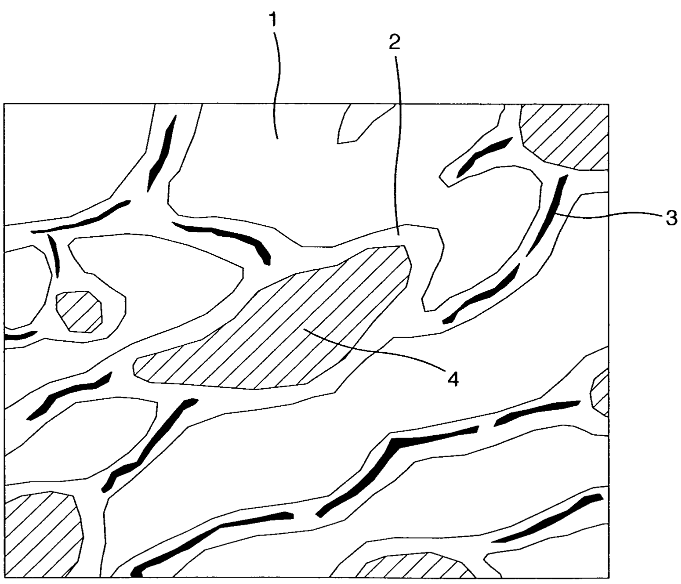
(54) **Copper-based sliding material**

(57) A copper-based sliding material consisting of: 5.0 to 25.0 mass % of Zn; 4.2 to 10.0 mass % of Bi; 2.0 to 7.0 mass % of Mn; 1.0 to 3.0 mass % of Si; 0.1 to 2.0 mass % of Sn; and the balance being Cu and unavoidable impurities is provided. The copper-based sliding material includes a single α-phase matrix (1, 2), a Mn-Si compound (3) and a Bi-particle phase (4). The Mn-Si compound (3) and the Bi-particle phase (4) are dispersed in the single α-phase matrix (1, 2). The mass ratio of Sn to Bi is 0.024 to 0.200, preferably 0.050 to 0.140.

FIG. 1



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Description

Technical Field

[0001] The present invention relates to a sliding material used under severe conditions. Particularly, the present invention relates to a copper-based sliding material suitable for e.g. a floating bush for turbochargers in motor vehicles or the like, and having high productivity.

Background of the invention

[0002] In recent years, it has been becoming popular that an automotive engine is equipped with a turbocharger to increase the output thereof. Since the turbocharger has a structure to rotate a turbine at a high speed with high-temperature exhaust gas from an engine to drive a compressor, the operating conditions are extremely severe. Especially, when the engine is rotated at a high speed and then stopped immediately, oil supply to a floating bush is stopped, so that the temperature of the floating bush is elevated to higher than 300°C by heat conduction from a turbine casing. If the engine is restarted in this state, the turbine immediately approaches the highest rotation as high as 100,000 rpm. Since the supply of lubricant delays, however, lubrication effect falls in the stopped (dry-up) state. Specifically, the floating bush is required to have favorable resistance to seizing and abrasion even under the dry-up state at such a high temperature.

[0003] JP-A-03-215642 discloses, as a sliding material satisfying such requirements, high-strength brass composed of, by mass percent, 1 to 3.5% of Mn, 0.3 to 1.5% of Si, 10 to 25% of Zn, 5 to 18% of Pb, and the balance being Cu and unavoidable impurities. Here, Pb is uniformly dispersed in the whole structure and the matrix consists of a single α-phase. As another sliding material, JP-A-9-316570 discloses a manganese silicide high-strength brass which has a metal structure including β-phase controlled to be not more than 30% so that it can be subjected to cold plastic working. The manganese silicide high-strength brass is composed of, by mass percent, 0.3 to 5% of Mn, 0.3 to 3% of Si, 15 to 37% of Zn, 0.3 to 4% of Bi, and the balance being Cu and unavoidable impurities.

[0004] The former sliding material has favorable performances in resistance to seizing and abrasion. Since it contains Pb, however, it has a problem in view of recent environmental concerns. The latter sliding material includes a hard β-phase in the matrix, and thus the resistance to abrasion is improved. When it is used under severe conditions, such as a floating bush for a turbocharger, problems is still left in resistance to seizing. To eliminate the above-described defects, JP-A-2004-137512 proposes a copper-based sliding material consisting of, by mass percent, 15 to 25% of Zn, 4.2 to 10% of Bi, 2 to 7% of Mn, 1 to 3% of Si, and the balance being Cu. The matrix is composed of a single α-phase, and the eutectic structure composed of the α-phase and a Mn-Si compound, and Bi particles are dispersed in the matrix (see paragraphs [0009] to [0010]).

Summary of the invention

[0005] In the copper-based alloy disclosed in JP-A-2004-137512, a Bi-particle phase is dispersed in the matrix of single α-phase by adding a large quantity of Bi. If the copper-based alloy is manufactured by a continuous casting method or the like suited to mass production, cracks possibly generate due to the stress during the drawing from the mold. When the stress during the drawing is applied to the copper-based alloy, it is considered that shear generates at the interface between the α-phase and the Bi-particle phase since the quantity of deformation differs between the α-phase having a high ductility and the Bi-particle phase having little ductility. The shear becomes the starting point of the cracking. Although the alloy cracking can be reduced by lowering the drawing rate, the productivity lowers, and therefore there is no advantage to adopt the continuous casting method for mass production. Furthermore, if the Zn content is increased to make the matrix of the copper-based alloy be composed of the α-phase and β-phase structure, the strength of the matrix is increased and the ductility thereof is lowered. Thus, the cracking of the copper-based alloy unlikely occurs. However, it is not preferable as the sliding material for supporting a shaft rotating at a high speed in a high-temperature atmosphere such as for a turbocharger, since the strength of the copper-based alloy becomes excessively high, and resistance to seizing and conformability (which is such property that the alloy deforms by itself, while it contacts the counter shaft, to reduce stress generated by the contact) are lowered. Although the alloy cracking can be reduced by reducing the Bi content in the copper-based alloy disclosed in JP-A-2004-137512, the content of Bi, which is a lubricating component, becomes excessively low, and the sliding property required in the sliding material for supporting a high-speed rotating shaft in a high-temperature atmosphere, such as for turbochargers, cannot be satisfied.

[0006] The invention is made in taking the above-described situations in consideration. It is an object of the invention to provide a copper-based sliding material that has improved resistance to seizing, abrasion and friction and conformability as well as improved productivity, even if it is used under severe conditions under which it is rotated at a high speed in a high-temperature atmosphere, such as a floating bush for a turbocharger for motor vehicles or the like.

[0007] In order to achieve the above-described object, the invention provides a copper-based sliding material consisting of 15.0 to 25.0 mass % of Zn, 4.2 to 10.0 mass % of Bi, 2.0 to 7.0 mass % of Mn, 1.0 to 3.0 mass % of Si, 0.1 to 2.0 mass % Sn, and the balance being Cu and unavoidable impurities. The copper-based sliding material includes a single α-phase matrix in which a Mn-Si compound and a Bi-particle phase are dispersed, and the mass ratio of Sn to Bi is 0.024 to 0.200.

[0008] In an embodiment, the mass ratio of Sn to Bi is 0.050 to 0.140.

[0009] By adding Sn, a laminar "Sn-containing α-phase" is formed so as to surround the periphery of each crystal grain having the α-phase and the Bi-particle phase in the copper-based alloy structure. The ductility of each phase in the copper-based alloy structure is in the order of: α-phase > "Sn-containing α-phase" > Bi-particle phase. Therefore, when a stress is applied, the "Sn-containing α-phase" plays a role to relax the deformation difference between the Bi-particle phase and the α-phase. This will function to relax the shear stress due to the difference in deformation between the α-phase and the Bi-particle phase generated during drawing in the continuous casting process, and thereby, it is considered that the problem of alloy cracking can be prevented.

[0010] The reason why the contents of Sn and Bi are determined to be, respectively, 0.1 to 2.0 mass % and 4.2 to 10 mass % and the mass ratio of Sn to Bi is determined to be 0.024 to 0.200 (more preferably 0.050 to 0.140) is as follows. If the mass ratio of Sn to Bi is smaller than 0.024, the amount of "Sn-containing α-phase" formed in the periphery of the Bi-particle phase is small and cannot completely surround the periphery of the Bi-particle phase, and the effect of preventing the cracking in the copper-based alloy is reduced. On the other hand, if the mass ratio of Sn to Bi exceeds 0.200, the effect of preventing cracking in the copper-based alloy is also reduced. This is presumed because the melt Bi-particle phase before solidified reacts with the "Sn-containing α-phase" in the cooling process of the copper-based alloy to form a Bi-Sn hypoeutectic alloy at their interface. The Bi-Sn hypoeutectic alloy contains less Sn than the Bi-Sn eutectic composition (Bi-43 mass % Sn having a melting point at about 140°C). In this composition range, the melting point lowers according to increase in the Sn content. In the manufacture using a continuous casting method, the copper-based alloy is drawn after cooling it to lower than a temperature at which the Bi-particle phase, of which melting point is lowest in the copper-based alloy structure (the melting point is about 270°C), is fully solidified. When the mass ratio of Sn to Bi is high so as to form the Bi-Sn hypoeutectic alloy, cracking of the alloy will occur. The stress of drawing will apply in the state wherein a part of the Bi-Sn hypoeutectic alloy is not solidified. When the mass ratio of Sn to Bi is not more than 0.200, it is presumed that copper-based alloy will not suffer from cracking, since little or no Bi-Sn hypoeutectic alloy is formed.

[0011] The reason why a Mn-Si compound is dispersed in the single α-phase matrix in the copper-based sliding material is because the high-temperature strength of the material increases. A copper-based sliding material used in a high-temperature region, such as a floating bush for a turbocharger, is required to have high-temperature strength as well as ductility. Although the strength of the copper-based alloy is lowered with the elevation of temperature, the high-temperature strength of the copper-based alloy can be increased by dispersing a Mn-Si compound whose strength is not lowered even at the high temperature.

[0012] Bi is added as a lubricating component for improving the resistance to seizing of the copper-based sliding material. Little Bi dissolves in the copper-alloy matrix, but is dispersed in the matrix as fine particles. If the quantity of the added Bi is less than 4.2 mass %, the effect to increase the resistance to seizing is insufficient for the copper-based sliding material to support the shaft rotating at a high speed in a high-temperature atmosphere. If the quantity is more than 10 mass %, the strength of the copper-based sliding material is lowered.

[0013] Mn improves the strength of the matrix. It forms hard compounds having excellent sliding properties, such as Mn-Si compounds (mainly Mn_5Si_3), and contributes to improve the resistance to abrasion and seizing, friction properties, and strength at a high temperature. If the quantity of the added Mn is less than 2.0 mass %, the effect cannot be obtained. If the quantity is more than 7.0 mass %, the addition of Zn described below becomes hardly useful.

[0014] Si forms Mn-Si compounds with Mn as described above, and similar to Mn, it serves to improve the resistance to abrasion and seizing, friction properties, and strength at a high temperature. The quantity of the added Si is determined by the composition of the Mn-Si compound. The compound is formed when the mass ratio of Mn to Si is 1:0.3. Therefore, the content of Si may be at least 0.6 mass %. However, since all Si does not form a compound with Mn, the minimum quantity of added Si in the present invention is determined to be 1.0 mass %. If the quantity exceeds 3.0 mass %, the quantity of free Si becomes excessive and causes the copper-based sliding material brittle.

[0015] Zn improves the strength of the matrix, resistance to abrasion, and corrosion resistance to lubricants. The quantity of the added Zn will be mentioned. According to the Cu-Zn binary phase diagram, if the quantity of Zn is not more than 38.0 mass %, the matrix becomes a single α-phase, and if the quantity of Zn exceeds 38.0 mass %, a β-phase appears. However, when a third element dissolved in the α-phase or the β-phase, such as Mn and Si in the present invention, is added, Mn and Si change the structure of the matrix as if the quantity of the added Zn were increased. Therefore, the quantity of the added Zn is determined to be at most 25.0 mass % in consideration of the contents of Mn and Si. Thus, the matrix can be made to be a single α-phase. However, if the content of Zn is less than 15.0 mass %, the effect of the resistance to abrasion and corrosion to lubricants is degraded.

Brief description of the drawing

[0016]

Fig. 1 is a schematic diagram of a microstructure of a copper-based sliding material according to the present invention.

Detailed description of the invention

[0017] Fig. 1 shows a schematic diagram of a structure of the alloy of the present invention. As shown in Fig. 1, a Mn-Si compound 3 and a fine Bi-particle phase 4 are uniformly dispersed in a matrix of the single α-phase 1, 2 in the copper-based alloy. The single α-phase is composed of a primary crystal α-phase 1 that contains little Sn, and a laminar "Sn-containing α-phase" 2 surrounding the periphery of the primary crystal α-phase 1. The Bi-particle phase 4 is also surrounded by the laminar "Sn-containing α-phase" 2. The Mn-Si compound 3 is distributed in the laminar "Sn-containing α-phase" 2. Thus, the "Sn-containing α-phase" 2 is formed between the α-phase having a high ductility and the Bi-particle phase 4 having little ductility. It is considered that the "Sn-containing α-phase" 2 plays a role to relax the shear stress due to difference in the quantity of deformation between the Bi-particle phase 4 and the α-phase 1 when an external force is applied, and this functions to prevent alloy cracking generating between the α-phase 1 and the Bi-particle phase 4 during drawing in the continuous casting process. The copper-based sliding material shown in Fig. 1 contains 20.0 mass % of Zn, 3.5 mass % of Mn, 1.5 mass % of Si, 6.5 mass % of Bi, and 0.47 mass % of Sn.

Examples

[0018] Alloys having the compositions of Examples 1 to 11 according to the present invention, and alloys having the compositions of Comparative Examples 21 to 25, shown in Table 1, were subjected to an alloy cracking evaluation test in which the presence or absence of the alloy cracking on the surface of the copper-based alloys cast under the casting conditions and drawn at drawing rate shown in Table 2 were visually observed. The presence or absence of the alloy cracking is shown in Table 1.

[Table 1]

	No.	Composition (by mass %)						Mass ratio of Sn to Bi	Alloy cracking evaluation	
									Drawing rate	
		Cu	Zn	Mn	Si	Bi	Sn		20 mm/sec.	30 mm/sec.
Examples	1	Bal.	20.0	4.5	2.0	10.00	2.00	0.200	absence	presence
	2	Bal.	20.0	4.5	2.0	4.20	0.84	0.200	absence	presence
	3	Bal.	20.0	4.5	2.0	4.20	0.10	0.024	absence	presence
	4	Bal.	20.0	4.5	2.0	10.00	0.24	0.024	absence	presence
	5	Bal.	20.0	4.5	2.0	6.50	0.73	0.112	absence	absence
	6	Bal.	20.0	4.5	2.0	5.00	0.70	0.140	absence	absence
	7	Bal.	20.0	4.5	2.0	8.00	1.12	0.140	absence	absence
	8	Bal.	20.0	4.5	2.0	8.00	0.40	0.050	absence	absence
	9	Bal.	20.0	4.5	2.0	5.00	0.25	0.050	absence	absence
	10	Bal.	25.0	4.5	2.0	6.50	0.73	0.112	absence	absence
	11	Bal.	15.0	4.5	2.0	6.50	0.73	0.112	absence	absence
Comparative examples	21	Bal.	20.0	4.5	2.0	10.00	0.10	0.010	presence	presence
	22	Bal.	20.0	4.5	2.0	5.00	0.10	0.020	presence	presence
	23	Bal.	20.0	4.5	2.0	8.00	2.00	0.250	presence	presence
	24	Bal.	20.0	4.5	2.0	4.20	1.00	0.238	presence	presence
	25	Bal.	20.0	4.5	2.0	6.50	-	-	presence	presence

[Table 2]

Casting machine	Horizontal continuous casting machine
Melting temperature	1200°C
Retention temperature	1050°C
Cooling speed	150°C/sec
Die	Carbon
Drawing temperature	250°C
Drawing speed	20 mm/sec, 30 mm/sec
Casting size	ϕ20 mm

[0019] All of Examples 1 to 11 are within the scope of the present invention, among which Examples 1 to 9 contains substantially mean values of the contents range of Zn, Mn and Si. Examples 10 and 11 contain Zn, respectively, at the upper and lower limits, and other components at mean value of the content range. Among Examples 1 to 11, Examples 1 to 4 are examples wherein the invention according to claim 1 is embodied. Examples 1 and 2, Examples 3 and 4, and Examples 5, 10 and 11 adopted "the mass ratio of Sn to Bi" is the upper limit, the lower limit, and the median value, respectively. On the other hand, Examples 6 to 9 are examples wherein the invention according to claim 2 is embodied. Examples 6 and 7, and Examples 8 and 9 adopted "the mass ratio of Sn to Bi" at the desirable upper limit and lower limit, respectively.

[0020] On the other hand, all of Comparative Examples 21 to 25 are out of the scope of the present invention. Comparative Examples 21 and 22 and Comparative Examples 23 and 24 adopted "the mass ratio of Sn to Bi" to be lower than lower limit and higher than upper limit, respectively. Comparative Example 25 does not contain Sn, which is the feature of the present invention.

[0021] As shown by the lists in the "Alloy cracking evaluation" column of Table 1, no cracking generated in any of Examples 1 to 11 when the alloys were drawn at the drawing rate of 20 mm/sec. While the cracking occurred in any of Comparative Example 25 which does not contain Sn used in conventional sliding materials, and Comparative Examples 21 to 24 which contain Sn and Bi, but the mass ratio of Sn to Bi is beyond the scope of the present invention. Furthermore, even when the alloys were drawn at higher drawing rate of 30 mm/sec, no cracking occurred in any of Examples 5 to 11 which have the mass ratio of Sn to Bi being more preferable 0.050 to 0.140.

[0022] More specifically explaining, the copper-based alloy of any of Examples 1 to 11 according to the present application has a structure, in which the Mn-Si compound and the fine Bi-particle phase are uniformly distributed in the matrix composed of the single α-phase as shown in Fig. 1. Furthermore, the matrix is composed of the single α-phase and the periphery of the α-phase primary crystal grain containing little Sn is completely surrounded by a laminar "Sn-containing α-phase". The Bi-particle phase is also surrounded by the laminar "Sn-containing α-phase". The Mn-Si compound is distributed in the laminar "Sn-containing α-phase". Thus, the "Sn-containing α-phase" having intermediate ductility is present between the α-phase having a high ductility and the Bi-particle phase having little ductility. Therefore, it is considered that the "Sn-containing α-phase" plays the role to relax shear stress due to the difference in the quantity of deformation between the Bi-particle phase and the α-phase when an external force is applied, and this functions to prevent alloy cracking between the α-phase and the Bi-particle phase when the alloy is drawn in the continuous casting process. On the other hand, since the mass ratio of Sn to Bi was low in Comparative Examples 21 and 22, alloy cracking generated. It is considered to have occurred since the quantity of the "Sn-containing α-phase" formed in the periphery of the Bi-particle phase is small, and cannot completely surround the periphery of the Bi-particle phase, so that shear is generated by the difference in the quantity of deformation when an external force was applied.

[0023] On the other hand, alloy cracking occurred in the Comparative Examples 23 and 24, since the mass ratio of Sn to Bi is high. This is considered because the Bi-particle phase reacts with the "Sn-containing α-phase" in the cooling process to form a Bi-Sn hypoeutectic alloy at the interface, and a part of the Bi-Sn hypoeutectic alloy is not yet solidified even when the copper alloy is drawn. Since the stress of drawing is applied to the copper alloy in the state, alloy cracking occurred. When the mass ratio of Sn to Bi is not more than 0.200, it is considered that little or no Bi-Sn hypoeutectic alloy is formed and the copper alloy cracking was prevented.

[0024] As is seen from the above results of the alloy-cracking test, controlling the mass ratio of Sn to Bi forms the laminar "Sn-containing α-phase" between the α-phase having a high ductility in the single α-phase matrix and the Bi-particle phase having little ductility, and it is considered that the "Sn-containing α-phase" plays a role to relax the difference in ductility between the Bi-particle phase and the α-phase and functions to relax shear stress applied to the interface of the phases due to the difference in the quantity of deformation between the α-phase and the Bi-particle phase generated when the alloy is drawn in the continuous casting process. Thereby, the problem of generating alloy cracking can be prevented. Although exemplary copper-based alloy compositions are shown, the inventors have confirmed that copper-based alloy compositions within the scope of the present invention also have the same effect as the effect of Examples.

[0025] The copper-based sliding material according to the present invention is not only used in floating bushes for the turbochargers of motor vehicles and the like, but also widely applied to bearings in general which require, for example, resistance to seizing and abrasion, friction properties and conformability under severe conditions.

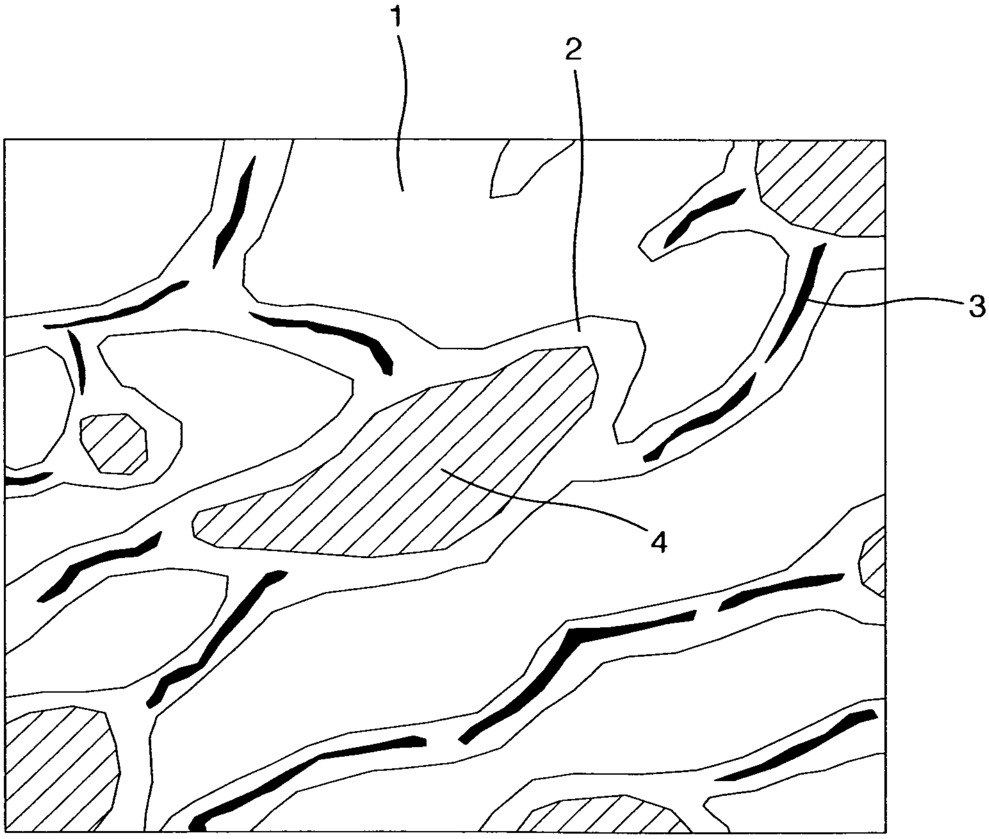
Claims

1. A copper-based sliding material consisting of:

15.0 to 25.0 mass % of Zn,
4.2 to 10.0 mass % of Bi,
2.0 to 7.0 mass % of Mn,
1.0 to 3.0 mass % of Si,
0.1 to 2.0 mass % of Sn, and
the balance being Cu and unavoidable impurities,
the copper-based sliding material including a single a-phase matrix (1, 2), a Mn-Si compound (3) and a Bi-particle phase (4), the Mn-Si compound (3) and the Bi-particle phase (4) being dispersed in the single α-phase matrix (1, 2), and the mass ratio of Sn to Bi being 0.024 to 0.200.

2. The copper-based sliding material according to claim 1, wherein the mass ratio of Sn to Bi is 0.050 to 0.140.

FIG. 1



REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 3215642 A **[0003]**
- JP 9316570 A **[0003]**
- JP 2004137512 A **[0004] [0005]**