



(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
11.02.2009 Bulletin 2009/07

(51) Int Cl.:
B22C 9/10 (2006.01) **B22C 1/00** (2006.01)
B22C 9/24 (2006.01) **B22D 29/00** (2006.01)

(21) Application number: **07743674.9**

(86) International application number:
PCT/JP2007/060239

(22) Date of filing: **18.05.2007**

(87) International publication number:
WO 2007/135995 (29.11.2007 Gazette 2007/48)

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC MT NL PL PT RO SE SI SK TR
Designated Extension States:
AL BA HR MK RS

(72) Inventors:
• **YAOKAWA, Jun**
Sendai-shi, Miyagi 9808577 (JP)
• **ANZAI, Koichi**
Sendai-shi, Miyagi 9808577 (JP)
• **YAMADA, Youji**
Iwata-shi, Shizuoka 4388501 (JP)

(30) Priority: **18.05.2006 JP 2006138879**

(71) Applicants:
• **National University Corporation Tohoku University**
Sendai Miyagi 980-8577 (JP)
• **Yamaha Hatsudoki Kabushiki Kaisha**
Iwata-shi, Shizuoka 438-8501 (JP)

(74) Representative: **Grünecker, Kinkeldey, Stockmair & Schwanhäusser**
Anwaltssozietät
Leopoldstrasse 4
80802 München (DE)

(54) **METHOD FOR PRODUCING SALT CORE FOR CASTING AND SALT CORE FOR CASTING**

(57) When forming an expendable salt core (2) by die casting, first, a salt mixture containing at least a potassium salt and a sodium salt is melted by heating to obtain a melt. Subsequently, the temperature of the melt is decreased to set the melt in a semi-solidified (solid-

liquid coexisting) state. The melt in the semi-solidified state is injected into a metal mold for an expendable salt core under a high pressure and solidified. After solidification, the obtained expendable salt core is taken out of the metal mold.

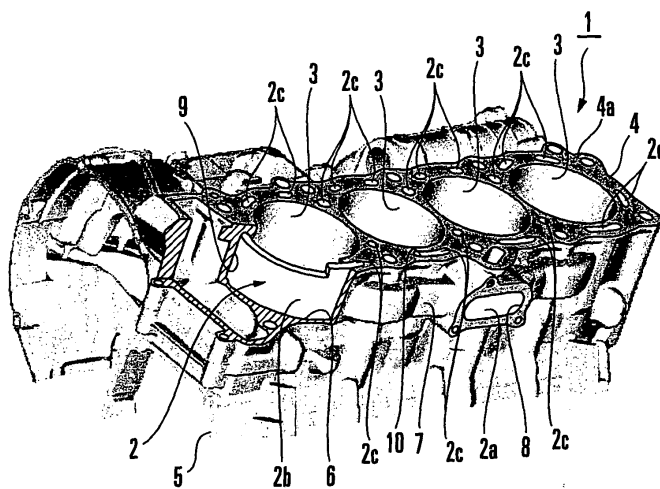


FIG. 1

Description

Technical Field

5 **[0001]** The present invention relates to a method of manufacturing a water soluble expendable salt core for casting, and an expendable salt core for casting.

Background Art

10 **[0002]** As is known well, casting such as aluminum high pressure die casting (HPDC) is a technique that injects a molten aluminum alloy into a metal mold at high speed under a high pressure to cast a near-net-shape structure. In this casting, when molding a cast product having a hollow structure, e.g., a water cooling water jacket in the closed-deck type cylinder block of an internal combustion engine, an expendable core is used. The expendable core used in such a case must have a strength that can withstand a high pressure and high temperature because it may be subject to a large impact or impulse force fluctuation upon collision of a molten metal injected from the gate at high speed mold filling and because a high static compressive casting pressure is applied until solidification completion. After casting, the expendable core is removed from the cast product. When the cast product has a complicated internal structure, if a generally used phenol resin bonded sand core is used as the expendable core, it is not easy to remove. In contrast to this, a water soluble expendable salt core is available as the expendable core that can be removed by dissolution with, e.g., high-temperature water (reference 1: Japanese Patent Laid-Open No. 48-039696, reference 2: Japanese Patent Laid-Open No. 50-136225, and reference 3: Japanese Patent Laid-Open No. 52-010803).

20 **[0003]** The expendable salt core as described above is formed by using a salt mixture of, e.g., sodium carbonate (Na_2CO_3), potassium chloride (KCl), and sodium chloride (NaCl), melting these components, and molding. Hence, a high static compressive casting pressure resistance is obtained, and workability and stability of dimension accuracy in casting are improved.

Disclosure of Invention

Problems to be Solved by the Invention

30 **[0004]** When an expendable fused salt core is formed by melting a salt and casting, however, the formation of a shrinkage cavity, micro-porosity, small heat crack, and the like would be caused in the salt core due to a change in volume such as solidification shrinkage occurring in the solidification process. It is therefore not easy to mold the expendable fused salt core conforming to the mold precisely. Also, depending on the composition of the respective components, the resultant melting point is 700°C or more, which is not suitable for molding by melting. In this manner, with the prior art, an expendable fused salt core cannot be manufactured easily by casting using a molten salt.

35 **[0005]** The present invention has been made to solve the above problems, and has as its object to facilitate manufacture of a water soluble expendable salt core for casting which is formed of a salt cast product obtained by molding after melting salts such as sodium and potassium.

Means of Solution to the Problems

40 **[0006]** A method of manufacturing an expendable salt core for casting according to the present invention comprises at least the first step of heating a salt mixture containing at least a potassium salt and a sodium salt to form a melt in a solid-liquid coexisting state in which a solid phase and a liquid phase coexist, the second step of charging the melt in the solid-liquid coexisting state into a core mold, and the third step of solidifying the melt in the mold to mold an expendable salt core for casting. Therefore, at the point when the mold is charged with the melt, the melt is partly solidified.

45 **[0007]** An expendable salt core for casting according to the present invention is molded by heating a salt mixture containing at least a potassium salt and a sodium salt to form a melt in a solid-liquid coexisting state in which a solid phase and a liquid phase coexist, charging the melt in the solid-liquid coexisting state into a core mold, and solidifying the melt in the mold. This expendable salt core for casting comprises, e.g., a core to mold a water jacket for water cooling a closed-deck type cylinder block of engine.

Effect of the Invention

50 **[0008]** According to the present invention, an expendable salt core is cast using a melt in a solid-liquid coexisting state. Therefore, a water soluble expendable salt core for casting made of a salt cast product, which is molded by melting salts such as sodium and potassium, can be manufactured easily.

Brief Description of Drawings

[0009]

- 5 Fig. 1 is a perspective view of a cylinder block which is cast using an expendable salt core for casting according to the present invention;
 Fig. 2 is a photograph which is obtained by a metallographic microscope (optical microscope) and shows the state of the solidification structure of a salt core 2;
 Fig. 3 is a graph showing the temperature dependence of the solid phase ratio of a melt in a semi-solidified state;
 10 Fig. 4 is a photograph of a solidification structure obtained by a scanning electron microscope when a salt mixture with a composition containing a large amount of chloride is melted and molded, and solidified without stirring;
 Fig. 5 is a photograph of a solidification structure obtained by a scanning electron microscope when a salt mixture with a composition containing a large amount of carbonate is melted and molded, and solidified without stirring;
 Fig. 6A is a graph showing the bending strengths of bending test pieces of sample Nos. 1 to 9;
 15 Fig. 6B is a graph showing the bending strengths of bending test pieces of sample Nos. 10 to 12;
 Fig. 6C is a graph showing the bending strengths of bending test pieces of sample Nos. 13 to 17;
 Fig. 7A is a graph showing the bending strengths of bending test pieces of sample Nos. 18 to 23;
 Fig. 7B is a graph showing the bending strengths of bending test pieces of sample Nos. 24 to 27;
 Fig. 8 is a phase diagram showing the relationship among the cation ratio of potassium ions vs. sodium ions, the anion ratio of carbonate ions vs. chloride ions, and the liquidus temperature;
 20 Fig. 9A is a view showing the state of a test piece used for bending strength measurement;
 Fig. 9B is a sectional view showing part of the test piece used for bending strength measurement;
 Fig. 10 is a view for explaining bending strength measurement;
 Fig. 11 is a photograph for explaining pressure measurement portions in the cavity of an expendable salt core during injection molding;
 25 Fig. 12 is a graph showing the measurement result of the pressure in the cavity of the expendable salt core during injection molding;
 Fig. 13 is a perspective view of another cylinder block which is cast using an expendable salt core for casting according to the present invention; and
 30 Fig. 14 is a photograph of an expendable salt core 1302 shown in Fig. 13.

Best Mode for Carrying Out the Invention

35 **[0010]** The embodiment of the present invention will be described hereinafter with reference to the drawings. First, how an expendable salt core for casting according to the embodiment of the present invention is used will be described with reference to Fig. 1. Fig. 1 is a partially cutaway perspective view of a closed-deck type cylinder block which is cast using the expendable salt core for casting according to the present invention. Referring to Fig. 1, reference numeral 1 denotes a closed-deck type cylinder block of engine, which is made of an aluminum alloy and cast using an expendable salt core 2 as an expendable salt core for casting according to the present invention. The cylinder block 1 is part of a
 40 water cooling 4-cycle 4-cylinder engine for a motorcycle which is molded into a predetermined shape by high pressure die casting (HDPC).

[0011] The cylinder block 1 shown in Fig. 1 integrally has four cylinder bores 3, a cylinder body 4 having the cylinder bores 3, and an upper crank case 5 extending downward from the lower end of the cylinder body 4. A lower crank case (not shown) is attached to the lower end of the upper crank case 5. The upper crank case 5, together with the lower
 45 crank case, rotatably, axially supports a crank shaft (not shown) through a bearing.

[0012] The cylinder body 4 is a so-called closed-deck-type cylinder body, and has a water jacket 6 which is formed in it using the expendable salt core 2. The water jacket 6 is formed to include a cooling water passage forming portion 7, cooling water inlet port 8, main cooling water passage 9, and communication passage 10. The cooling water passage forming portion 7 projects on one side of the cylinder body 4 and extends in the direction in which the cylinder bores 3
 50 line up. The cooling water inlet port 8 is formed in the cooling water passage forming portion 7. The main cooling water passage 9 is formed to communicate with a cooling water distribution passage (not shown) formed in the cooling water passage forming portion 7 and cover all the cylinder bores 3. The communication passage 10 extends upward in Fig. 1 from the main cooling water passage 9 and opens to a mating surface 4a with respect to a cylinder head (not shown) at the upper end of the cylinder body 4.

55 **[0013]** The water jacket 6 described above supplies cooling water flowing in from the cooling water inlet port 8 to the main cooling water passage 9 around the cylinder bores through the cooling water distribution passage, and guides the cooling water from the main cooling water passage 9 to a cooling water passage in the cylinder head (not shown) through the communication passage 10. Since the water jacket 6 is formed in this manner, the cylinder body 4 is covered with

the ceiling wall (the wall that forms the mating surface 4a) of the cylinder body 4 except that the communication passage 10 of the water jacket 6 opens to the mating surface 4a at the upper end to which the cylinder head is connected. Hence, a closed-deck-type arrangement is formed.

[0014] The expendable salt core 2 to form the water jacket 6 has a shape identical to that obtained by integrally connecting the respective portions of the water jacket 6. In Fig. 1, the cylinder body 4 is partly cut away to facilitate understanding of the shape of the expendable salt core 2 (the shape of the water jacket 6).

[0015] The expendable salt core (salt core for casting) 2 according to this embodiment is formed using a plurality of types of salts such as sodium carbonate, sodium chloride, and potassium chloride by, e.g., die casting in a solid-liquid coexisting state such as a semi-solidified state into the shape of the water jacket 6. The expendable salt core 2 may be formed by heating a salt mixture containing at least a potassium salt and a sodium salt to form a melt in a solid-liquid coexisting state in which a solid phase and liquid phase coexist, charging the melt into a core mold, and solidifying the melt in the mold. A method of manufacturing the expendable salt core 2 will be described later in detail.

[0016] Note that the expendable salt core 2 can be formed by a casting method other than die casting, e.g., gravity casting. In formation of the expendable salt core 2 which employs die casting, first, a mixture consisting of a plurality of salts (to be described later) is melted by heating to obtain a melt. Then, the temperature of the melt is decreased to set the melt in a semi-solidified (solid-liquid coexisting) state. The melt in the semi-solidified state is injected into an expendable salt core forming metal mold under a high pressure and solidified. After solidification, the obtained expendable salt core 2 is taken out from the mold.

[0017] As shown in Fig. 1, in the expendable salt core 2, the passage forming portion 2a which forms the cooling water inlet port 8 and the cooling water distribution passage, an annular portion 2b which surrounds the four cylinder bores 3, and a plurality of projections 2c extending upward from the annular portion 2b are formed integrally. The projections 2c form the communication passage 10 of the water jacket 6. As is conventionally known, the expendable salt core 2 is supported at a predetermined position in the metal mold (not shown) by a core print (not shown) during casting, and is removed by dissolution with hot water or vapor after casting.

[0018] To remove the expendable salt core 2 after casting, the cylinder block 1 may be dipped in a dissolution tank (not shown) which contains dissolving liquid consisting of hydrochloric acid and hot water. When dipping the cylinder block 1 in the dissolving liquid, the passage forming portion 2a and the projections 2c exposed to the mating surface 4a, of the expendable salt core 2 come into contact with the dissolving liquid and dissolve. The dissolved portions expand gradually until all the portions dissolve finally. In this core removing process, to promote dissolution of the expendable salt core 2 left in the water jacket 6, hot water or vapor may be sprayed under a pressure from a hole. In the expendable salt core 2, in place of the projections 2c, a core print may be inserted in portions where the projections 2c are to be formed.

[0019] If hydrochloric acid is used in the process of removing the expendable salt core 2 from the cylinder block 1 as a cast product, carbon dioxide gas foams. The foam provides a stirring function and promotes dissolution effectively. As the expendable salt core 2 contains potassium carbonate and sodium carbonate, when it dissolves in water, the resultant water exhibits alkaline. This alkali state poses problems such as corrosion of the cylinder block 1 as an aluminum cast product. Regarding this problem, corrosion of the cylinder block can be prevented by adding hydrochloric acid to control pH to near 7.

[0020] The method of manufacturing the expendable salt core 2 will now be described in detail. First, a case will be described in which the melt is not injected (pressure-injected) under a high pressure as in die casting, but flowed (poured) into the metal mold to manufacture the expendable salt core 2 (gravity casting). To form the expendable salt core 2 of this embodiment, first, sodium carbonate, potassium carbonate, sodium chloride, and potassium chloride are mixed and heated until they are melted, thus preparing a melt of a salt mixture. For example, when the salts are mixed such that a molar ratio $XK^+ (= [K^+]/([Na^+] + [K^+]) \times 100)$ of potassium ions in the entire cations is 33 mol% and that a molar ratio $YCO_3^{2-} (= [CO_3^{2-}]/([CO_3^{2-}] + [Cl^-]) \times 100)$ of carbonate ions in the entire anions is 67 mol%, the salt mixture dissolves at 647°C. For example, the salt mixture described above may be put in an alumina crucible and dissolved in an electric furnace.

[0021] Subsequently, when the temperature of the salt mixture accommodated in the crucible reached 647°C, which is a liquidus temperature or more, the crucible was taken out from the electric furnace and air-cooled. The cooling speed was 0.3°C to 1.2°C per sec. At this time, the salt mixture in the crucible was stirred with an alumina stirrer with a rotation speed of 3 rps, and was poured into the metal mold when the temperature of the melt of the salt mixture was 638°C. When the melt of the salt mixture is 638°C, the melt is in a semi-solidified state in which the solid phase and liquid phase coexist. The melt in this state is charged into a metal mold for an expendable salt core and solidified, and is taken out from the metal mold after solidification. In the above description, after the salt mixture was heated to set it in a liquid-phase-only state, it was cooled, thus obtaining a melt in a solid-liquid coexisting state. However, the present invention is not limited to this. A melt in the semi-solidified state may be obtained by heating the salt mixture to a semi-solidification temperature.

[0022] The thus obtained expendable salt core 2 had a strength (bending strength) of as high as 21.4 MPa to 24.6 MPa. The solidification structure of the expendable salt core 2 comprised fine crystal particles as is seen from the

photograph shown in Fig. 2 which is obtained by a metallographic microscope. As shown in Fig. 3, in the salt mixture having the above composition, the solid-liquid coexisting temperature range is as wide as about 60°C, and the temperature dependence of the solid phase ratio is small in the solid phase ratio range of 0 to 40%. Hence, a melt of a salt mixture with an even solid-liquid coexisting state can be obtained easily. In this manner, according to the manufacturing method of this embodiment, the expendable salt core 2 can be manufactured without strict temperature control or isothermal holding. The range of a temperature where the melt entirely exhibits a solid phase to a temperature where the melt entirely exhibits a liquid phase, in other words, the temperature range where the solid-liquid coexisting state is maintained, changes depending on the composition ratio of the respective components of the salt mixture.

[0023] As described above, in the process of cooling the dissolved melt, when the melt temperature reaches the liquidus temperature (melting point) or less, a plurality of solid phase particles are formed and dispersed in the remaining liquid phase. At this time, when stirring the melt in the semi-solidified state, a state can be obtained in which the solid phase is dispersed more evenly in the liquid phase. Note that stirring is not always necessary.

[0024] As an example, Fig. 4 shows a photograph of a solidification structure obtained by a scanning electron microscope (SEM) when a salt mixture with a composition of 0 mol% of XK^+ ($= [K^+]/([Na^+] + [K^+]) \times 100$) and 10 mol% of YCO_3^{2-} ($= [CO_3^{2-}]/([CO_3^{2-}] + [Cl^-]) \times 100$) is formed by melting and solidified without stirring. With this composition, primary crystals tend to grow into dendrites, and accordingly stirring is preferred. As another example, Fig. 5 shows an SEM photograph of a solidification structure obtained when a salt mixture with a composition of 0 mol% of XK^+ ($= [K^+]/([Na^+] + [K^+]) \times 100$) and 70 mol% of YCO_3^{2-} ($= [CO_3^{2-}]/([CO_3^{2-}] + [Cl^-]) \times 100$) is formed by melting and solidified without stirring. With this composition, primary crystals tend to crystallize, and accordingly stirring may not be necessary.

[0025] As described above, stirring may be performed although it is not necessary. Stirring can decrease the temperature distribution in the salt mixture in the solid-liquid coexisting state, so that a salt mixture with an even solid phase ratio can be obtained more easily. Also, because stirring can miniaturize and spheroidize solid phase particles in the salt mixture in the solid-liquid coexisting state, the moldability is improved. When molding a core with a high solid phase ratio, stirring is preferred. When mechanical stirring is to be performed, a ceramic stirrer which is resistant to corrosion by a molten salt may be employed.

[0026] When core molding is initiated in the semi-solidified state having the characteristic features as described above, the amount of solidification shrinkage occurring in the solidification process can be suppressed. Thus, a shrinkage cavity, micro-porosity, small heat crack, or the like which is formed in the expendable salt core can be suppressed. As the amount of solidification shrinkage can be suppressed, the expendable salt core can be molded true to the mold more precisely. When casting is initiated in the completely molten state as in the conventional case, the amount of solidification shrinkage is large, so that a shrinkage cavity, micro-porosity, small heat crack, or the like is formed often. The semi-solidification method can suppress these defects, thus improving the strength.

[0027] According to the melting molding method, the amount of solidification shrinkage of the core to be molded is larger than the amount of shrinkage of the metal mold. When molding a cylindrical annular core such a water jacket in a cylinder, a shrinkage cavity, micro-porosity, small heat crack, or the like may be formed in the expendable salt core. Depending on the case, the expendable salt core may be broken in the mold. In contrast to this, as described above, use of a melt in the semi-solidified state can reduce the ratio of solidification shrinkage. As a result, a cylindrical annular core such as a water jacket can be formed.

[0028] In injection molding using a melt, if the melt is injected with an injection force larger than the machine clamp force of the mold, the melt is scattered from the parting surface, i.e., so-called flushing occurs. In contrast to this, in injection molding using a melt in a solid-liquid coexisting state, the leading end of the melt solidifies immediately. Even if the melt is injected with an injection force larger than the mold cavity projected area, flushing does not occur. Therefore, during solidification shrinkage of the melt, a large injection pressure can be applied to replenish the melt, so that the shrinkage cavity can be eliminated. When the melt in the solid-liquid coexisting state is employed, casting can be performed at a temperature lower than that required by the completely molten state. This can improve the workability and decrease the heat load to the casting mold.

[0029] Different from metals, salt is not oxidized. Even when stirring described above is performed in the atmosphere, no oxide is caught in the melt. Thus, the melt can be stirred easily for a long period of time. Even when molding an annular shape from a semi-solidified state, no oxide skin is formed on a confluence-junction portion on the opposite side of the melt which separates from the gate into two groups in the circumferential direction. Hence, cold shut does not occur, so that separation at the bonding portion does not occur after molding.

[0030] In order to obtain the solid-liquid coexisting state, the melt is cooled from the molten state to a semi-solidified range, thus achieving the solid-liquid coexisting state. However, the present invention is not limited to this. For example, a salt mixture in the solid phase may be heated to a semi-molten range so that a solid-liquid coexisting state is obtained. A solid powder salt (salt mixture) may be added to a molten salt so that a solid-liquid coexisting state is obtained. Alternatively, a molten salt may be added to a preheated solid salt (salt mixture) so that a solid-liquid coexisting state is obtained.

[0031] In the above description, a case is described in which sodium carbonate, potassium carbonate, sodium chloride,

EP 2 022 577 A1

and potassium chloride are mixed such that the molar ratio $XK^+ (= [K^+]/([Na^+] + [K^+]) \times 100)$ of potassium ions in the entire cations is 33 mol% and that the molar ratio $YCO_3^{2-} (= [CO_3^{2-}]/([CO_3^{2-}] + [Cl^-]) \times 100)$ of carbonate ions in the entire anions is 67 mol%. However, the present invention is not limited to this. For example, when the salt mixture has any one of the compositions shown in the following Tables 1 and 2, casting using a melt in a semi-solidified state is possible. In any case, the salt mixture is formed of only potassium ions, sodium ions, chloride ions, and carbonate ions.

[0032] Table 1 also shows the measurement results (maximum bending loads) of the bending strengths of the fabricated test pieces, and Table 2 also shows the measurement results (maximum bending strengths) of the bending strengths of the fabricated test pieces. Tables 1 and 2 are identical except that representations of the measurement results are different. The state of the bending load and that of the bending strength are shown in Figs. 6A to 6C and Figs. 7A and 7B in the form of bar graphs. The concentration of each ion is measured according to the analysis method determined by the rules of ion chromatograph analysis of JIS standard K0127.

[0033]

Table 1

Sample Number	Cation Ratio mol%		Anion Ratio mol%		Liquidus Temperature °C	Molding Temperature °C	Bending Load N		
	XNa ⁺	XK ⁺	YCl ⁻	YCO ₃ ²⁻			1st Time	2nd Time	3rd Time
1	67	33	33	67	647	638	2566	2947	2574
2	70	30	40	60	649	632	3229	3192	3274
3	70	30	30	70	665	648	3430	3158	2916
4	60	40	40	60	615	597	3021	2190	2382
5	60	40	30	70	630	619	2150	2662	2606
6	100	0	50	50	675	648	2852	4149	3322
7	100	0	30	70	753	740	3037	2535	3108
8	80	20	50	50	645	625	2526	2566	2350
9	80	20	30	70	704	678	2662	2606	2606
10	70	30	60	40	605	588	2105	3067	3177
11	50	50	30	70	604	592	2566	2347	2268
12	60	40	20	80	652	642	2290	1295	2338
13	90	10	70	30	652	635	2670	818	787
14	75	25	70	30	575	572	2424	2532	1460
15	40	60	40	60	575	565	779	668	904
16	100	0	10	90	827	821	970	1126	1112
17	60	40	10	90	685	671	1474	1533	1630
18	33	67	67	33	648	638	2048	1901	1609
19	40	60	60	40	620	606	1002	1769	1402
20	40	60	70	30	643	630	1426	1763	1410
21	30	70	70	30	655	638	1897	1345	1850
22	30	70	60	40	630	620	1354	657	1096
23	50	50	50	50	590	575	1208	910	1243
24	50	50	80	20	630	622	1394	231	821
25	40	60	80	20	652	644	424	348	625
26	60	40	70	30	602	589	1761	1553	1152
27	20	80	50	50	595	588	1290	1368	1135

[0034]

Table 2

Sample Number	Cation Ratio ol%		Anion Ratio mol%		Liquidus Temperature °C	Molding Temperature °C	Bending Strength MPa		
	XNa ⁺	XK ⁺	YCl ⁻	YCO ₃ ²⁻			1st Time	2nd Time	3rd Time
1	67	33	33	67	647	638	21.4	24.6	21.4
2	70	30	40	60	649	632	26.9	26.6	27.3
3	70	30	30	70	665	648	28.6	26.3	24.3
4	60	40	40	60	615	597	25.2	18.3	19.9
5	60	40	30	70	630	619	17.9	22.2	21.7
6	100	0	50	50	675	648	23.8	34.6	27.7
7	100	0	30	70	753	740	25.3	21.1	25.9
8	80	20	50	50	645	625	21.0	21.4	19.6
9	80	20	30	70	704	678	22.2	21.7	21.7
10	70	30	60	40	605	588	17.5	25.6	26.5
11	50	50	30	70	604	592	21.4	19.6	18.9
12	60	40	20	80	652	642	19.1	10.8	19.5
13	90	10	70	30	652	635	22.3	6.8	6.6
14	75	25	70	30	575	572	20.2	21.1	12.2
15	40	60	40	60	575	565	6.5	5.6	7.5
16	100	0	10	90	827	821	8.1	9.4	9.3
17	60	40	10	90	685	671	12.3	12.8	13.6
18	33	67	67	33	648	638	17.1	15.8	13.4
19	40	60	60	40	620	606	8.4	14.7	11.7
20	40	60	70	30	643	630	11.9	14.7	11.7
21	30	70	70	30	655	638	15.8	11.2	15.4
22	30	70	60	40	630	620	11.3	5.5	9.1
23	50	50	50	50	590	575	10.1	7.6	10.4
24	50	50	80	20	630	622	11.6	1.9	6.8
25	40	60	80	20	652	644	3.5	2.9	5.2
26	60	40	70	30	602	589	14.7	12.9	9.6
27	20	80	50	50	595	588	10.8	11.4	9.5

[0035] Fig. 8 shows the relationship (Phase diagram of the Na-K-Cl-CO₃ system) among the cationic ratio of potassium ions, the anionic ratio of carbonate ions, and the melting temperature (liquidus temperature). Fig. 8 shows the correspondence between the respective compositions shown in Table 1 and sample numbers. Fig. 8 also shows the liquidus temperature of NaCl when K⁺ is 0 mol% and CO₃²⁻ is 0 mol%, that of KCl when Na⁺ is 0 mol% and CO₃²⁻ is 0 mol%, that of Na₂CO₃ when K⁺ is 0 mol% and Cl⁻ is 0 mol%, and that of K₂CO₃ when Na⁺ is 0 mol% and Cl⁻ is 0 mol%. In Fig. 8, thick lines represent eutectic lines.

[0036] As is apparent from Tables 1 and 2, Figs. 6A to 6C, Fig. 7A, Fig. 7B, and Fig. 8, the bending test results exhibit high bending strengths in a region where XK⁺ is 0 to 50 mol% and YCO₃²⁻ is 30 to 80 mol%. Also, the bending test results exhibit particularly high bending strengths in a region where XK⁺ is 0 to 40 mol% and YCO₃²⁻ is 50 to 70 mol%.

[0037] Measurement of the bending strength will be described. To measure the bending strength, a prismatic test piece with a predetermined size is fabricated. A load is applied to the test piece, and the bending load is obtained from the maximum load needed to break the test piece. Fabrication of the test piece will be described first. A rod-like test piece 901 as shown in Figs. 9A and 9B is formed using a predetermined metal mold. The employed metal mold is made of chrome molybdenum steel, e.g., SCM440H. Fig. 9A also shows riser portions 902 used when charging the metal mold with a melt in a semi-solidified state. In measurement of the bending strength, the portions 902 are cut off. Fig. 9A is a side view, and Fig. 9B is a sectional view taken at the position b - b in Fig. 9A. The sizes indicated in Figs. 9A and 9B are design values of the metal mold.

[0038] To measure the bending strength of the rod-like test piece 901 fabricated in the above manner, first, as shown in Fig. 10, the test piece 901 is supported by two support portions 1001 arranged at the center of the test piece 901 at a gap of 50 mm from each other. In this support state, at the intermediate portion of the two support portions 1001, two load portions 1002 at a gap of 10 mm from each other apply a load to the test piece 901. The load to be applied to the test piece 901 is gradually increased. The load applied when the test piece 901 was broken was the bending load shown in Table 1.

[0039] A bending strength σ (MPa) can be obtained from a bending load P in accordance with an equation $\sigma = 3LP/BH^2$ where H is the length of the load direction in the section of the test piece, B is a length perpendicular to the load direction in the section of the test piece, and L is the distance from the support portions 1001 serving as fulcrums to the load portions 1002 where the load acts. Although the test piece 901 is formed by pouring the melt in the solid-liquid coexisting state into the metal mold, it is difficult to form a test piece completely free from flow marks or shrinkage cavity and having a shape completely coinciding with the size true to the mold. Therefore, the bending strength is calculated based on an approximation that the test piece has a rectangular section and that $H \approx 20$ mm, $B \approx 18$ mm, and $L = 20$ mm. Due to this approximation, the estimated strength is lower than the actual strength by approximately 0% to 20%. For example, it can be assumed that a test piece which is broken by a bending load of 1200N is stronger than an ideal test piece having a bending strength of 10 MPa.

[0040] A method of manufacturing another expendable salt core according to the embodiment of the present invention will be described. The following description exemplifies a case in which a mold (metal mold) is charged with a melt under a pressure to manufacture an expendable salt core 2 (die casting). As the crucible, a close-packed alumina crucible made of the same material as that of a Tamman tube is employed. A predetermined amount of salt mixture consisting of sodium carbonate, potassium carbonate, sodium chloride, and potassium chloride is put in the crucible, the crucible is placed in a heating furnace, and the temperature is raised. For the purpose of protection of the crucible, the temperature is raised gradually to reach the target temperature in about 14 hours.

[0041] The target temperature is set at a value higher than the liquidus temperature corresponding to the molar ratio of the salt mixture by 10 to 30°C. Once the temperature reaches the target temperature, it is held at the target temperature. The temperatures of the metal mold and injection sleeve are set to approximately 180 to 220°C. As the metal mold, one that can be heated to a mold temperature of about 250°C is preferable. Also, a metal mold is preferred the casting cavity of which can be eliminated by applying a casting injection pressure of as high as about 120 MPa at maximum.

[0042] Subsequently, the melt of the salt mixture which is molten in the crucible is dipped up with a dipper. Prior to dipping up, the dipper must be heated to about 500 to 600°C by a heating means such as a burner. As soon as the melt in the crucible is dipped up with the dipper, it is started to be gradually deprived of heat by the dipper. Thus, the temperature of the melt decreases to be lower than the liquidus temperature, thus providing the solid-liquid coexisting state. During dipping up, the melt is stirred as it is shaken in the moving dipper, and primary crystals are deposited to form particles. In this manner, during the process of transporting the melt from the crucible and pouring it into the injection sleeve, the melt of the salt mixture in the dipper is set in the solid-liquid coexisting state.

[0043] When pouring the melt of the salt mixture in the semi-solidified state into the injection sleeve in this manner, the semi-solidified state progresses in the sleeve as well. Subsequently, the melt is injected into the cavity under a high pressure. After charging with the melt, the casting pressure is continuously applied into the mold. For example, a pressure of 120 MPa in the pressure ratio of a hydraulic cylinder which advances the plunger is applied into the mold. In this process, the plunger is advanced to replenish solidification shrinkage that takes place during solidification, thus continuously applying the pressure of 120 MPa. The solidification time is about 65 to 75 sec. In the solidification process, the plunger is continuously moved forward as long as solidification shrinkage can be replenished, thus continuously applying the pressure of 120 MPa.

[0044] After charging the mold with the melt under the pressure and solidifying the melt in the above manner, the solidified expendable salt core is taken out from the mold. A push pin and return pin may be placed in the stationary mold so that when the mold is opened, the obtained salt core is released from the stationary mold well. The taken-out expendable salt core may be gradually cooled, and the cooled expendable salt core may be put in a dried container.

[0045] An example will be described regarding the manufacturing conditions and strength measurement result of the expendable salt core which is manufactured by injecting into a metal mold under a high pressure a melt of a salt mixture in a semi-solidified state in which the solid phase and liquid phase coexist.

[0046] The conditions are as follows.

(1) The test piece subjected to strength measurement had an almost rectangular solid shape in the same manner as in Figs. 9A and 9B.

(2) The melt was fabricated by mixing sodium carbonate, potassium carbonate, sodium chloride, and potassium chloride and melting them. The resultant melt was adjusted such that the molar ratio $XK^+ (= [K^+]/([Na^+] + [K^+]) \times 100)$ of potassium ions in the entire cations was 30 mol% and that a molar ratio $YCO_3^{2-} (= [CO_3^{2-}]/([CO_3^{2-}] + [Cl^-]) \times 100)$ of carbonate ions in the entire anions was 54 mol%.

(3) The liquidus temperature of the salt mixture is 630°C.

(4) The salt mixture contained in the crucible was dissolved by gradually raising the temperature to exceed the liquidus temperature of 630°C in 14 hours. Then, the dissolved melt was held at 640 to 660°C. The temperature was controlled automatically.

(5) The dipper was heated to 500 to 600°C.

(6) The melt was dipped up with the dipper and cooled in the dipper to 630°C or less, so that the melt was set in the semi-solidified state.

(7) The sleeve temperature and metal mold temperature were 180 to 220°C.

(8) When the temperature of the melt of the salt mixture was 620°C in the injection sleeve, the melt was injected into the metal mold under a high pressure as indicated by an injection curve to be described later. When the temperature of the melt of the mixture salt is 620°C, the melt is in the semi-solidified state in which the solid and liquid coexist.

[0047] To measure the pressure in the cavity, the pressures acting on the push pins provided to two portions, i.e., a gate portion 1101 shown in Fig. 11 and a portion 1102 inside the mold, were measured. The measured pressures were both about 60 MPa, as represented by the injection curves in Fig. 12. In Fig. 12, the solid line represents the measurement result obtained at the portion 1101, and the dashed line represents the measurement result obtained at the portion 1102. Since the injection start time point until immediately before (by about 5 sec) the solidification end point when the mold was opened, the pressures to be measured were about 60 MPa, thus maintained almost the same state. Then, at the mold opening time point, the pressures sharply decreased. Actually, the pressures to be measured gradually decrease, as shown in Fig. 12. This may be because the expendable salt core solidifies starting with its surface to interfere with the pressure from being transmitted well. A directional solidification state was exhibited in which the pressure inside the mold dropped prior to the pressure at the gate portion. As described above, the pressure of about 120 MPa was applied to the plunger. Part of the melt solidified into gel in the injection sleeve interfered with driving of the plunger. Accordingly, the pressure actually acting on the melt in the cavity was approximately 60 MPa.

[0048] In die casting of a metal such as aluminum, the melt has high thermal conductivity and requires a short solidification time. Hence, that portion of the melt which is located at the intermediate portion of the mold often solidifies before that portion of the melt which is located at the distal end of the mold. Then, the distal end of the mold may not be sufficiently replenished with the melt. In contrast to this, a molten salt has low thermal conductivity and requires a solidification time about three times that of aluminum. Accordingly, as shown in Fig. 12, an almost constant pressure can be continuously applied to the entire cavity until mold opening. In this manner, to apply a pressure evenly to the cavity until opening the mold, e.g., to always apply the same pressure to the cavity until mold opening or gradually change the pressure to apply to the cavity with the same change amount until mold opening, is the condition necessary to obtain a high strength.

[0049] Test pieces manufactured as described above were subjected to bending strength measurement in the same manner as described above. A high strength exceeding 40 MPa was obtained as shown in the following Tables 3 and 4. In general, a bending strength of about 20 to 37 MPa is obtained by a widely employed expendable salt core which is manufactured by sintering after press molding (reference 4: US3,963,818). According to this embodiment, a higher bending strength is obtained. With an expendable salt core which is manufactured by sintering after press molding, a complicated shape such as a water jacket cannot be formed. According to this embodiment, however, an expendable salt core with a complicated shape can be manufactured easily. As the expendable salt core of this embodiment is formed by solidifying a molten salt, the surface state of the expendable salt core reflects the surface state of the metal mold, so that a smooth surface can be obtained. Therefore, in a cast product using the expendable salt core according to this embodiment, a portion which is in contact with the expendable salt core is formed to be highly smooth.

[0050]

Table 3

Sample Number	Cation Ratio mol%		Anion Ratio mol%		Liquidus Temperature °C	Molding Temperature °C	Bending Load N		
	XNa ⁺	XK ⁺	YCl ⁻	YCO ₃ ²⁻			1st Time	2nd Time	3rd Time
28	70	30	67	54	630	620	4812	5251	5008

[0051]

Table 4

Sample Number	Cation Ratio mol%		Anion Ratio mol%		Liquidus Temperature °C	Molding Temperature °C	Bending Strength MPa		
	XNa ⁺	XK ⁺	YCl ⁻	YCO ₃ ²⁻			1st Time	2nd Time	3rd Time
28	70	30	67	54	630	620	40.1	43.8	41.7

[0052] Although a salt mixture of sodium carbonate, potassium carbonate, sodium chloride, and potassium chloride is used in the above description, the present invention is not limited to this. For example, potassium carbonate, sodium chloride, and potassium chloride may be mixed, or sodium carbonate, sodium chloride, and potassium chloride may be mixed. Alternatively, other salts such as sodium bromide, potassium bromide, sodium iodide, potassium iodide, calcium chloride, potassium nitrate, sodium nitrate, potassium sulfate, lithium sulfate, magnesium sulfate, sodium sulfate, barium carbonate, and calcium carbonate may be mixed. A reinforcing ceramic material or another reinforcing agent may be contained in the mixture.

[0053] Another example of how an expendable salt core for casting according to the embodiment of the present invention is used will be described with reference to Figs. 13 and 14. Fig. 13 is a partially cutaway perspective view of a cylinder block which is cast using an expendable salt core for casting according to the present invention. Referring to Fig. 13, reference numeral 1301 denotes an engine cylinder block which is made of an aluminum alloy and cast using an expendable salt core 1302 as an expendable salt core for casting according to the present invention. The expendable salt core 1302 is manufactured in the same manner as the expendable salt core 2 shown in Fig. 1. The cylinder block 1301 is part of a water cooling 4-cycle 1-cylinder engine for a motorcycle which is molded into a predetermined shape by die casting.

[0054] The cylinder block 1301 shown in Fig. 13 comprises a cylinder bore 1303 and a cylinder body 1304 having the cylinder bore 1303. Although not shown, a crank case is attached to the lower portion of the cylinder body 1304 and rotatably, axially supports a crank shaft through a bearing.

[0055] The cylinder body 1304 is a so-called closed-deck-type cylinder body, and has a water jacket 1306 which is formed in it using the expendable salt core 1302. The water jacket 1306 is formed to include a cooling water passage forming portion (not shown), a cooling water inlet port (not shown), a main cooling water passage 1309, and a communication passage 1310. The cooling water passage forming portion projects on one side of the cylinder body 1304. The cooling water inlet port is formed in the cooling water passage forming portion. The main cooling water passage 1309 is formed to communicate with a cooling water supply passage (not shown) formed in the cooling water passage forming portion and cover the cylinder bore 1303. The communication passage 1310 extends upward in Fig. 13 from the main cooling water passage 1309 and opens to a mating surface 1304a with respect to a cylinder head (not shown) at the upper end of the cylinder body 1304.

[0056] The water jacket 1306 described above supplies cooling water flowing in from the cooling water inlet port (not shown) to the main cooling water passage 1309 around the cylinder bore through the cooling water supply passage, and guides the cooling water from the main cooling water passage 1309 to a cooling water passage in the cylinder head (not shown) through the communication passage 1310. Since the water jacket 1306 is formed in this manner, the cylinder body 1304 is covered with the ceiling wall (the wall that forms the mating surface 1304a) of the cylinder body 1304 except that the communication passage 1310 of the water jacket 1306 opens to the mating surface 1304a at the upper end to which the cylinder head is connected. Hence, a closed-deck-type arrangement is formed.

[0057] The expendable salt core 1302 to form the water jacket 1306 has a shape identical to that obtained by integrally connecting the respective portions of the water jacket 1306, as shown in the photograph of Fig. 14 as well. In Fig. 13, the cylinder body 1304 is partly cut away to facilitate understanding of the shape of the expendable salt core 1302 (the shape of the water jacket 1306). Note that reference numeral 1311 denotes a passage for a cam shaft driving chain;

and 1312, a chain tensioner attaching hole.

[0058] The expendable salt core 1302 shown in Fig. 13 (Fig. 14) is formed using a plurality of types of salts such as sodium carbonate, sodium chloride, and potassium chloride by, e.g., die casting in a solid-liquid coexisting state such as a semi-solidified state into the shape of the water jacket 1306, in the same manner as the expendable salt core 2 described above. Note that the expendable salt core 1302 can be formed by a casting method other than die casting, e.g., gravity casting. In formation of the expendable salt core 1302 which employs die casting, first, a mixture consisting of a plurality of salts (to be described later) is melted by heating to obtain a melt. Then, the temperature of the melt is decreased to set the melt in a semi-solidified (solid-liquid coexisting) state. The melt in the semi-solidified state is injected into a metal mold for an expendable salt core under a high pressure and solidified. After solidification, the obtained expendable salt core is taken out from the metal mold.

[0059] As shown in Fig. 13, in the expendable salt core 1302, the cooling water passage forming portion (not shown) which forms the cooling water inlet port and cooling water supply passage, an annular portion 1302b which surrounds the cylinder bore 1303, and a plurality of projections 1302a extending upward from the annular portion 1302b are formed integrally. The projections 1302a form the communication passage 1310 of the water jacket 1306. As is conventionally known, the expendable salt core 1302 is supported at a predetermined position in the metal mold (not shown) by a core print (not shown in Fig. 13) during casting, and is removed by dissolution with hot water or vapor after casting.

[0060] To remove the expendable salt core 1302 after casting, the cylinder block 1301 may be dipped in a dissolution tank (not shown) which contains dissolving liquid consisting of hydrochloric acid, hot water, and the like. When dipping the cylinder block 1301 in the dissolving liquid, the cooling water inlet port of the cooling water passage forming portion (not shown) and the projections 1302a exposed to the mating surface 1304a, of the expendable salt core 1302 come into contact with the dissolving liquid and dissolve. The dissolved portions expand gradually until all the portions dissolve finally. In this core removing process, to promote dissolution of the expendable salt core 1302 left in the water jacket 1306, hot water or vapor may be sprayed under a pressure from a hole. In the expendable salt core 1302, in place of the projections 1302a, a core print may be inserted in portions where the projections 1302a are to be formed.

[0061] As described above, according to the present invention, the annular expendable salt core 1302 can be formed easily. Note that the region of the core print shown in the photograph of Fig. 14 is a region that projects upward from the mating surface 1304a of Fig. 13. Although the overflow, gate, runner, and biscuit portions shown in the photograph of Fig. 14 remain when casting the expendable salt core 1302, they are removed when using the expendable salt core 1302 for casting the cylinder block 1301.

[0062] The present invention can be suitably used as a core in casting such as aluminum die casting.

Claims

1. A method of manufacturing an expendable salt core for casting, **characterized by** comprising at least:

a first step of heating a salt mixture containing at least a potassium salt and a sodium salt to form a melt in a solid-liquid coexisting state in which a solid phase and a liquid phase coexist;
a second step of charging said melt in the solid-liquid coexisting state into a core mold; and
a third step of solidifying said melt in said mold to mold an expendable salt core for casting.

2. A method of manufacturing an expendable salt core for casting according to claim 1, **characterized in that** in said first step, said salt mixture is heated to be set in a liquid-phase-only state, and thereafter said salt mixture is cooled, thus forming said melt in the solid-liquid coexisting state.

3. A method of manufacturing an expendable salt core for casting according to claim 1, **characterized in that** in said second step and said third step, said mold is charged with said melt under a pressure and said melt is solidified.

4. A method of manufacturing an expendable salt core for casting according to claim 3, **characterized in that** said pressure is applied evenly until said mold is opened.

5. A method of manufacturing an expendable salt core for casting according to claim 1, **characterized in that** said salt mixture is formed of only potassium ions, sodium ions, chloride ions, and carbonate ions, and a molar ratio of said potassium ions in all the cations is 50 mol% at maximum and a molar ratio of carbonate ions in all the anions is 30 to 80 mol%.

6. A method of manufacturing an expendable salt core for casting according to claim 5, **characterized in that** in said salt mixture, the molar ratio of the potassium ions in all the cations is 40 mol% at maximum and the molar

ratio of carbonate ions in all the anions is 50 to 70 mol%.

7. An expendable salt core for casting, **characterized by**
being molded by heating a salt mixture containing at least a potassium salt and a sodium salt to form a melt in a solid-liquid coexisting state in which a solid phase and a liquid phase coexist, charging said melt in the solid-liquid coexisting state into a core mold, and solidifying said melt in said mold.
8. An expendable salt core for casting according to claim 7, **characterized in that**
said melt in the solid-liquid coexisting state is formed by heating said salt mixture to be set in a liquid-phase-only state, and thereafter cooling said salt mixture.
9. An expendable salt core for casting according to claim 7, **characterized in that**
said expendable salt core for casting is formed by charging said mold with said melt under a pressure and solidifying said melt.
10. An expendable salt core for casting according to claim 9, **characterized in that**
said pressure is applied evenly until said mold is opened.
11. An expendable salt core for casting according to claim 7, **characterized in that**
said salt mixture is formed of only potassium ions, sodium ions, chloride ions, and carbonate ions, and a molar ratio of the potassium ions in all cations is 50 mol% at maximum and a molar ratio of carbonate ions in all the anions is 30 to 80 mol%.
12. An expendable salt core for casting according to claim 11, **characterized in that**
in said salt mixture, the molar ratio of the potassium ions in all the anions is 40 mol% at maximum and the molar ratio of carbonate ions in all the cations is 50 to 70 mol%.
13. An expendable salt core for casting according to claim 7, **characterized in that**
said expendable salt core for casting comprises a core to mold a water jacket for water cooling of a closed-deck type cylinder block of engine.

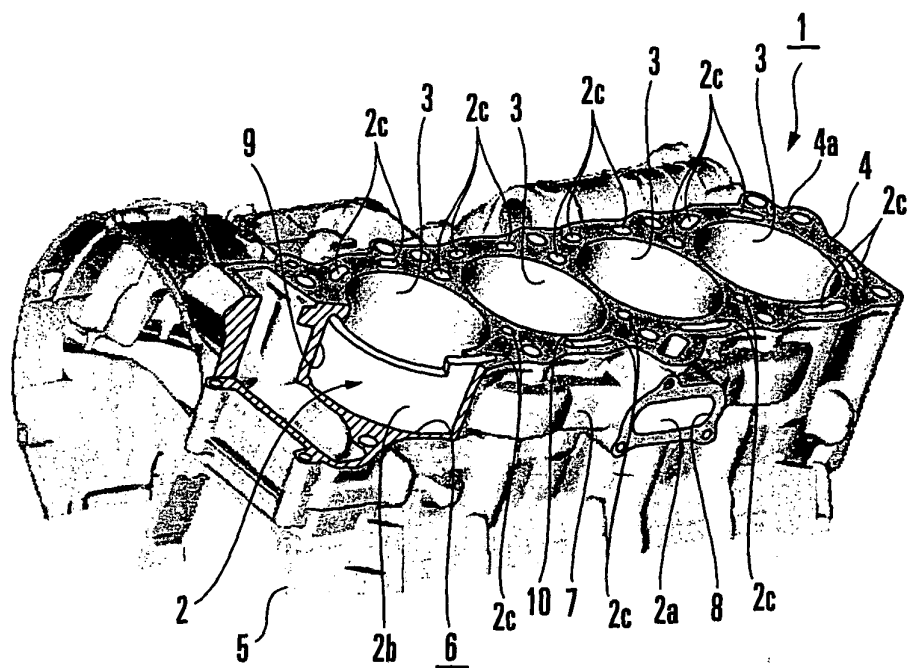


FIG. 1

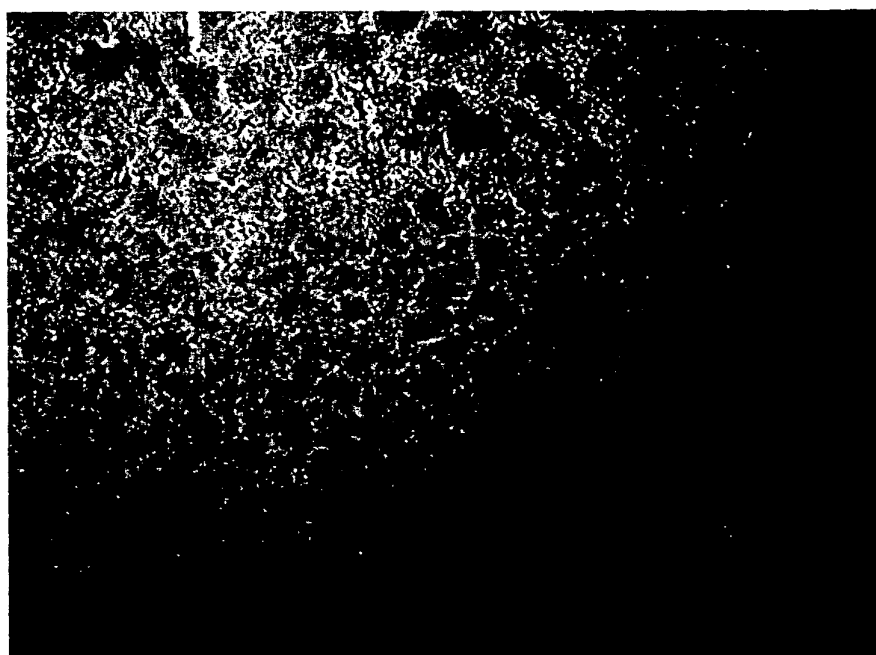


FIG. 2

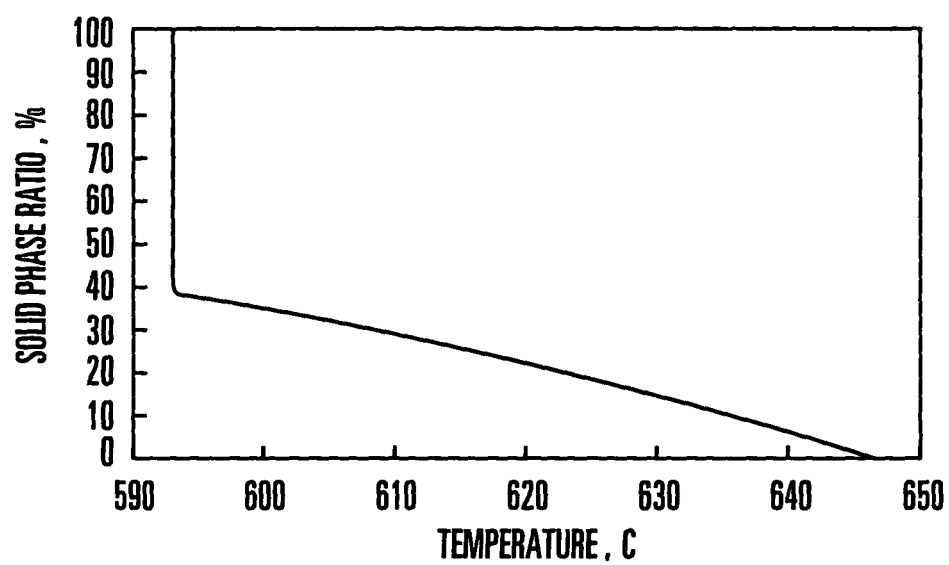


FIG. 3

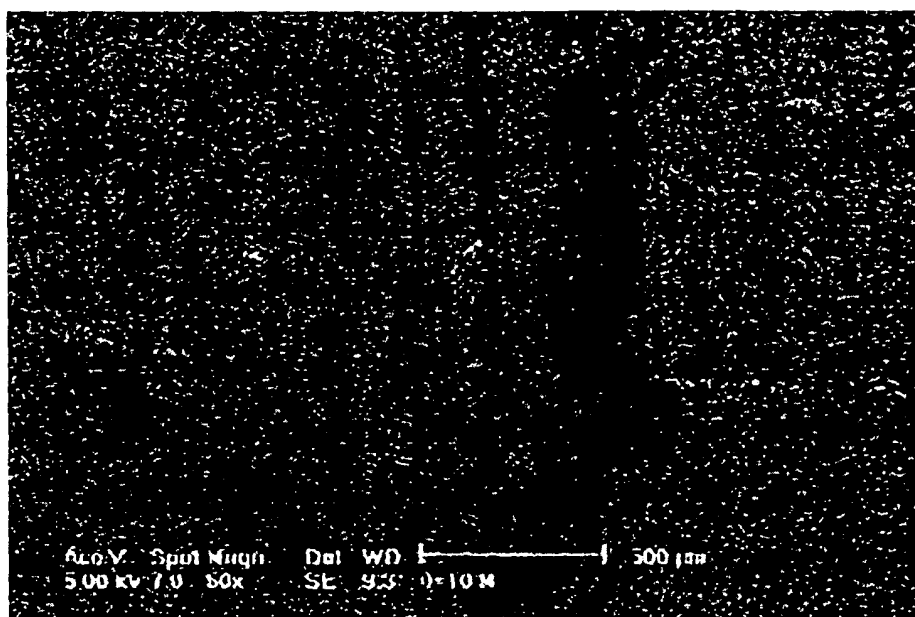


FIG. 4

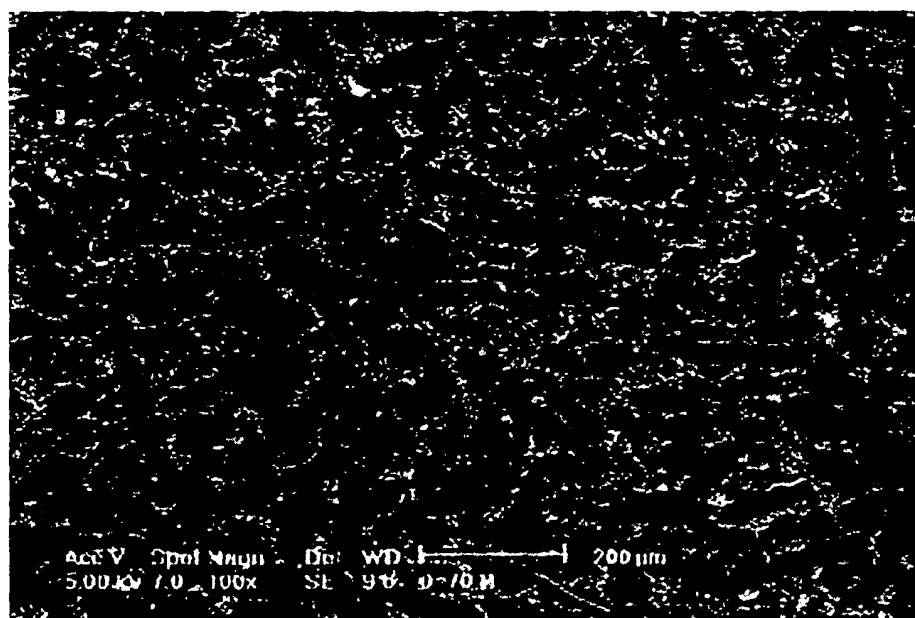


FIG. 5

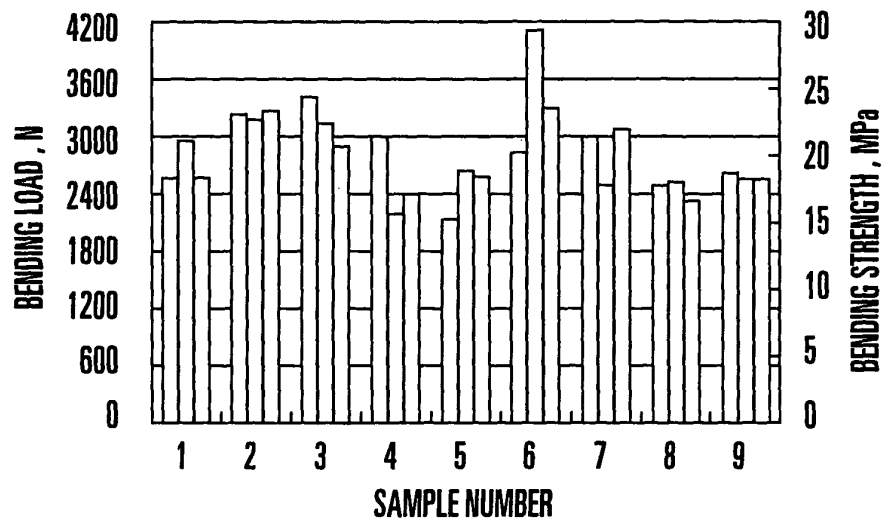


FIG. 6A

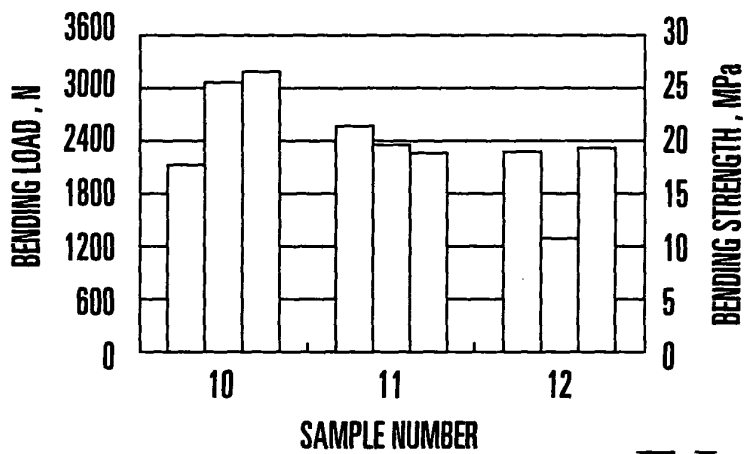


FIG. 6B

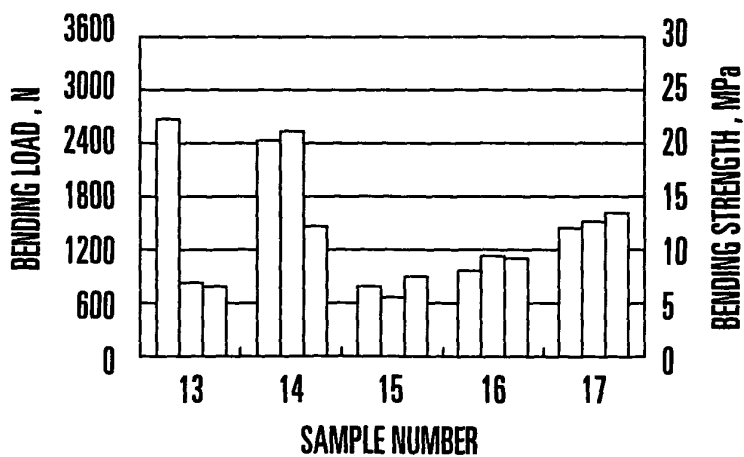


FIG. 6C

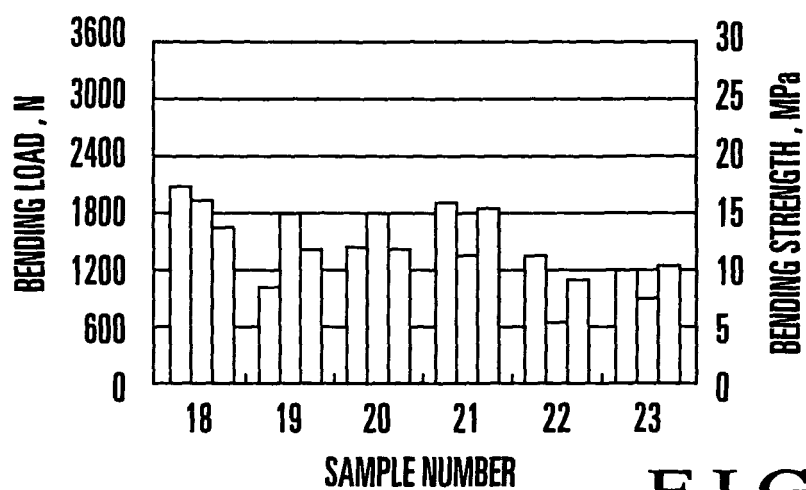


FIG. 7A

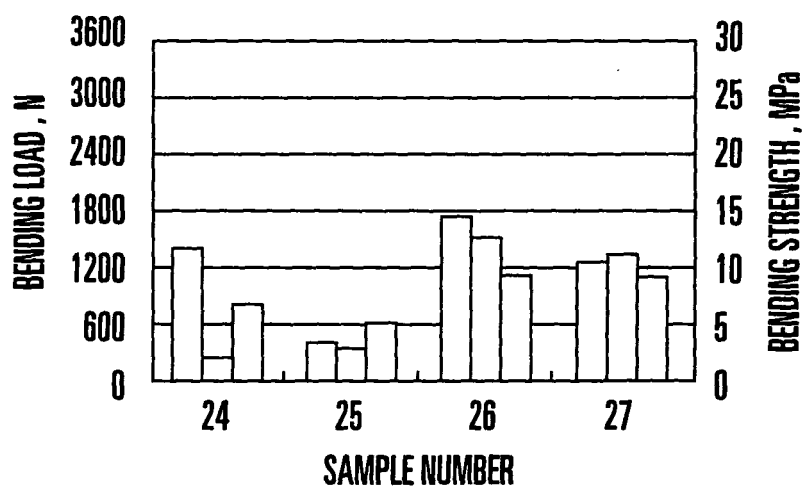


FIG. 7B

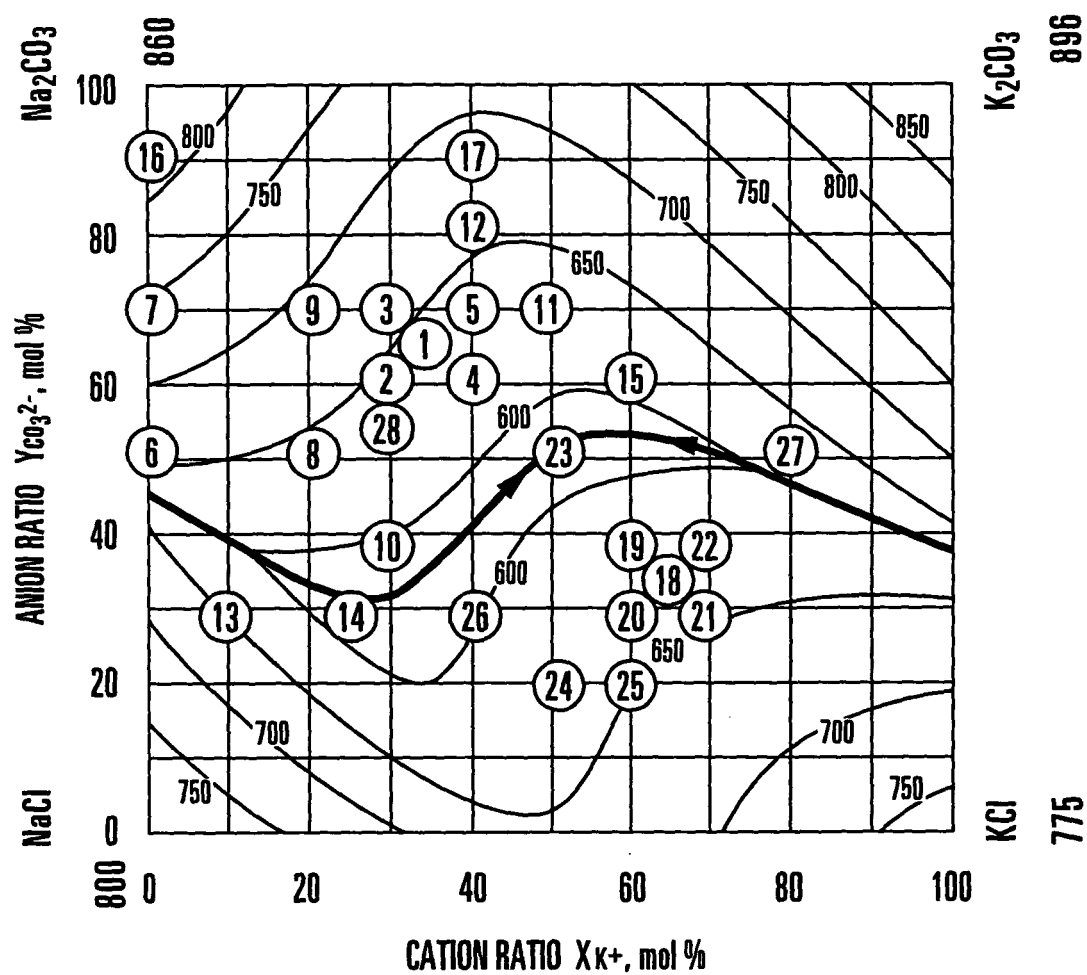


FIG. 8

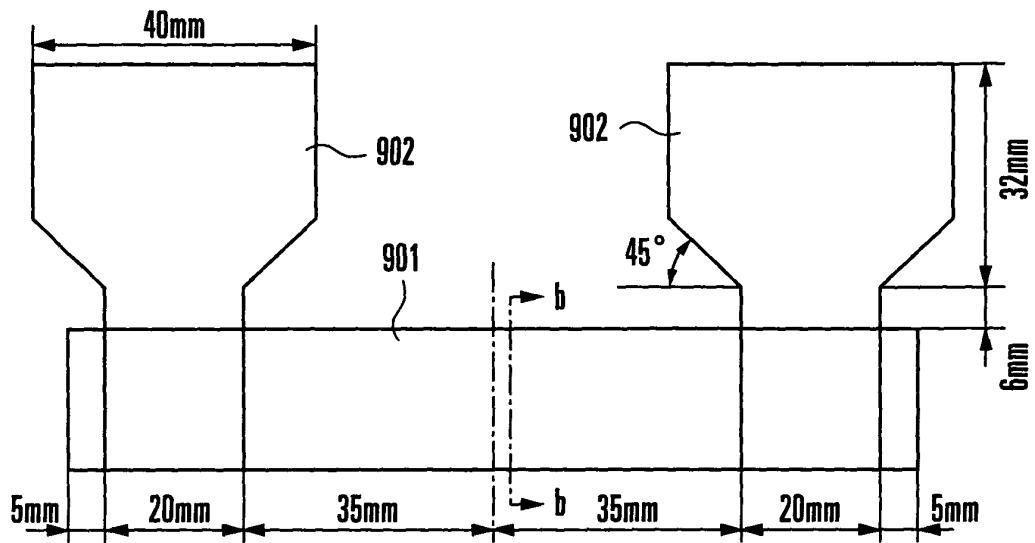


FIG. 9A

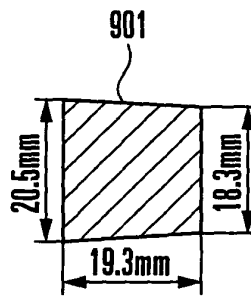


FIG. 9B

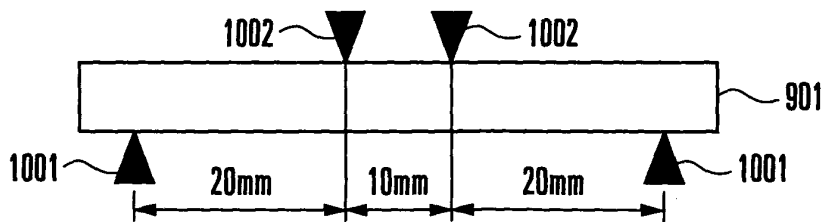


FIG. 10

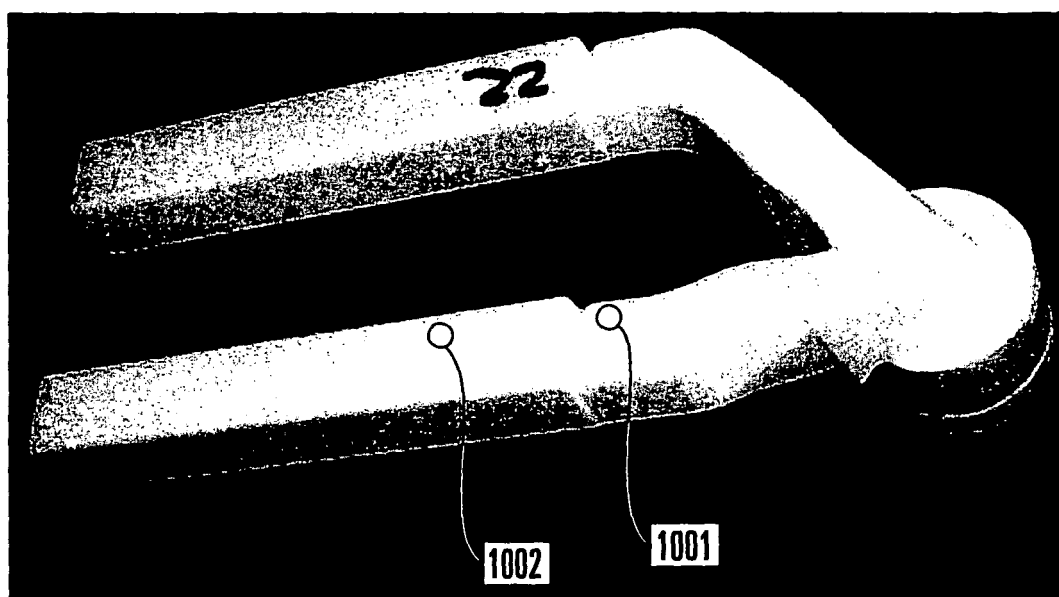


FIG. 11

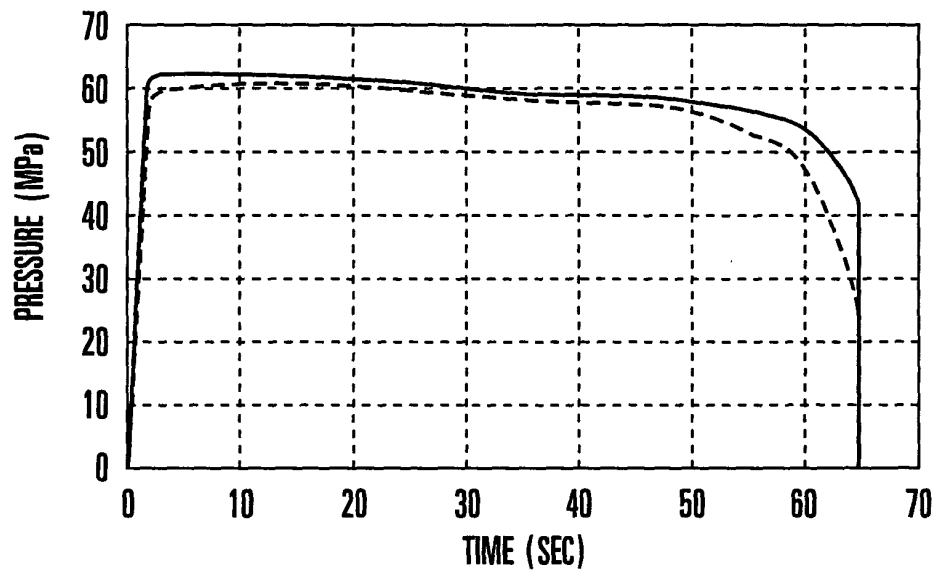


FIG. 12

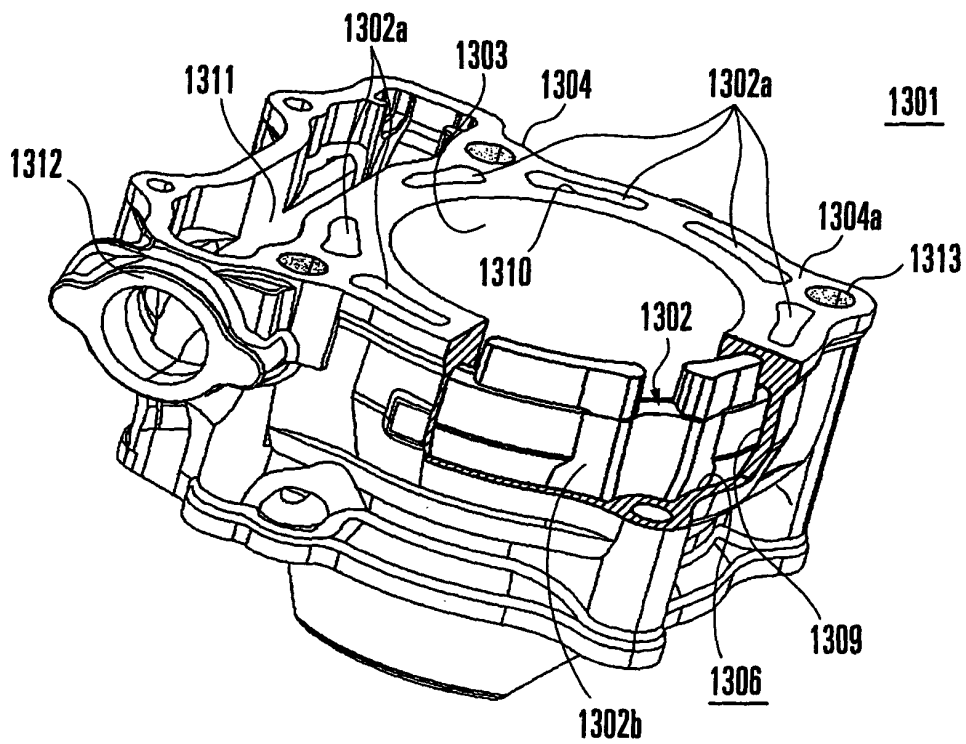


FIG. 13

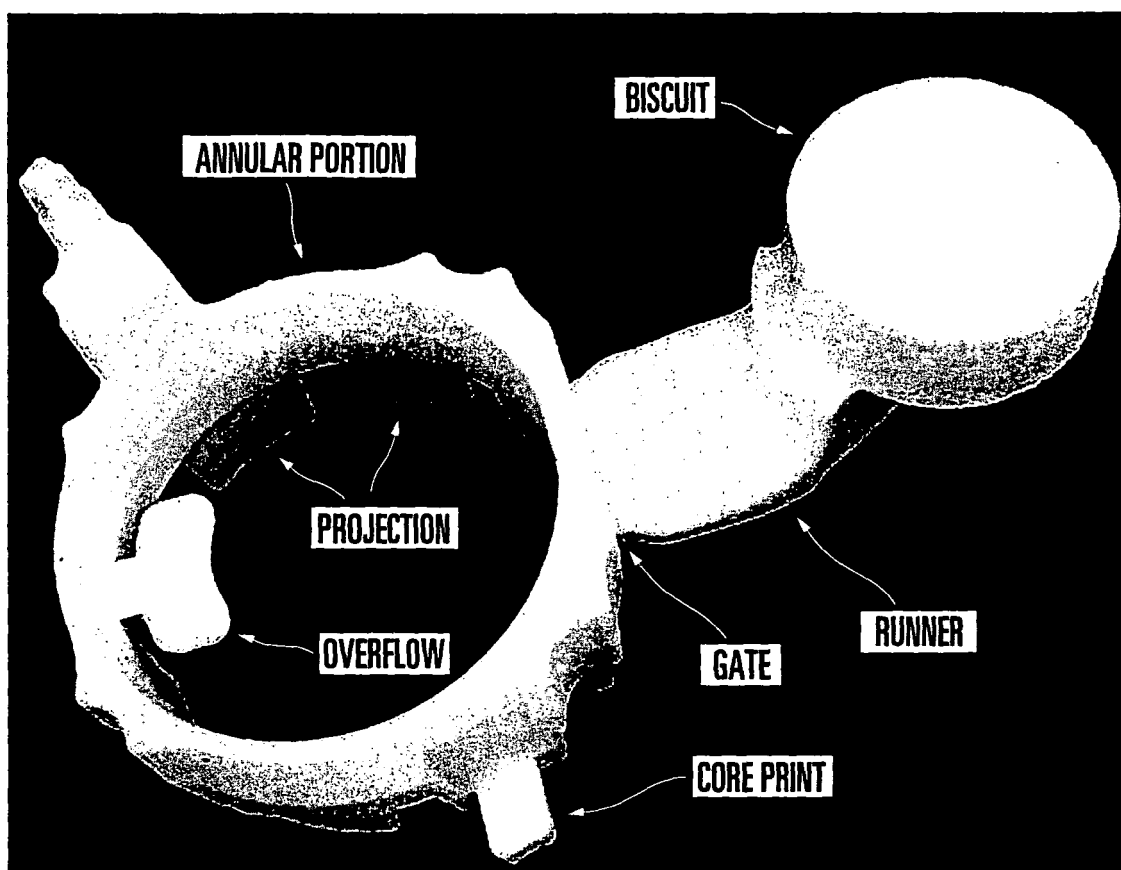


FIG. 14

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2007/060239

A. CLASSIFICATION OF SUBJECT MATTER

B22C9/10(2006.01)i, B22C1/00(2006.01)i, B22C9/24(2006.01)i, B22D29/00(2006.01)i

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)

B22C1/00-9/30, B22D29/00

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	1996-2007
Kokai Jitsuyo Shinan Koho	1971-2007	Toroku Jitsuyo Shinan Koho	1994-2007

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.
A	JP 53-14618 A (Hitachi, Ltd.), 09 February, 1978 (09.02.78), (Family: none)	1-13
A	JP 48-39696 B1 (Toyo Kogyo Kabushiki Kaisha), 26 November, 1973 (26.11.73), (Family: none)	1-13
A	JP 52-10803 B1 (Mitsubishi Heavy Industries, Ltd.), 26 March, 1977 (26.03.77), (Family: none)	1-13

☐ 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 July, 2007 (18.07.07)

Date of mailing of the international search report
31 July, 2007 (31.07.07)

Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 48039696 A [0002]
- JP 50136225 A [0002]
- JP 52010803 A [0002]
- US 3963818 A [0049]