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(54) Method for producing a high reactive alloy.

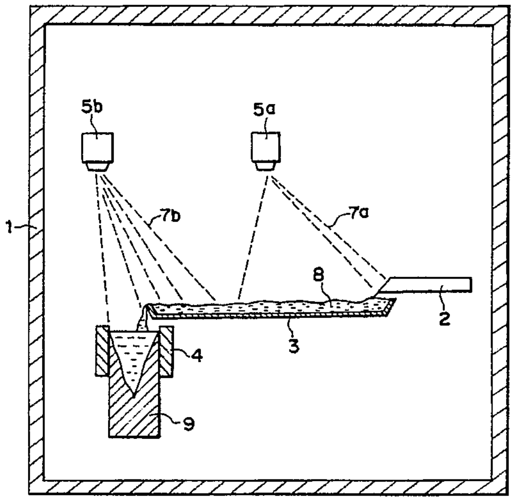
(57) A method for producing a high reactive alloy comprises the steps of producing an alloy containing a metal having a high melting point temperature and Aℓ, crushing the alloy to form granules of alloy, mixing said granules of alloy with metallic granules having a high melting point temperature, which has components other than components constituting the alloy, to form a mixture of the granules of alloy and the metallic granules, pressing the mixture into a compact to form the compact, and melting the compact by means of electron beams, Aℓ in the alloy being evaporated.

The alloy has a melting point temperature of 1650°C or more.

The metal is at least one selected from the group consisting of Ti, Nb, Mo, W, Zr, Ta and V.

The alloy is produced by means of an aluminium thermite process.

FIG.1



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METHOD FOR PRODUCING A HIGH REACTIVE ALLOY

The present invention relates to a method for producing a high reactive alloy containing elements having a high melting point temperature.

Methods for producing a high reactive alloy containing at least one metallic element having a high melting point temperature, which are presently used, are roughly divided into (a) a melting process, and (b) a powder sintering process.

The melting process is a process for converting alloy components to an alloy by melting the alloy components. As the melting furnace, an electron beam melting furnace, plasma melting furnace, vacuum arc melting furance, argon arc melting furnace or the like is used. In this process, granules or powders of alloy elements are pressed into a compact, and the compact thus produced is used as a consumable electrode. The consumable electrode is melted and an ingot is produced.

The above-mentioned melting process is widly used as a process for producing Ti alloy. In the case of producing Ti alloy containing a great amount of alloy elements each having a high melting point temperature respectively, however, this melting process has difficulties in that those alloy elements each having a high melting point temperature remain not melted, which makes it impossible to produce a uniform ingot.

Several processes for overcoming the above-mentioned difficulties have been reported so far. A process wherein alloy elements are processed into thin plates, and a consumable electrode is produced by sticking those thin plates together is disclosed in a Japanese Patent Publication Laid Open No. 120811/74. Another process wherein constituent elements in the form of granules or chips, whose forms are made sufficiently uniform, are mixed with each other and a consumable electrode is made by compressing the mixture thereof is disclosed in a Japanese Patent Publication Laid Open No. 251235/85. In those processes, however, melting materials themselves are expensive, and the cost, at which the consumable electrode is prepared, is very high. Therefore, those processes are not economical. As a result, produced ingots become expensive. On the other hand, as disclosed in a Japanese Patent Publication Laid Open No. 174838/85, yet another process wherein Nb-Ti alloy is produced by using pure Nb and pure Ti separately as feedstocks without forming compacts such as electrodes is pointed out. This process is a process wherein molten Ti is directly added to a pool of molten Nb and Ti and Nb are converted to an alloy. In this method, since a vapor pressure of the pure Ti is greatly high compared with that of the pure Nb, an evaporation loss of the pure Ti is large. In consequence, the yield of Ti is greatly lowered. Therefore, a problem such that it is very difficult to control the components of the alloy is further pointed out.

The powder sintering process is widely applied to alloys such as alloys of W, Mo and the like which have higher melting point tempertures than those used in the melting process. In this process, after powdery metals and alloys have been mixed with each other and the mixture thereof has been pressed into a compact, the compact is sintered and formed into a compact. This process has disadvantages such that the material powders are expensive and impurities are liable to be included into the compact due to conversion of metals and alloys to powders.

It is an object of the present invention to provide a method for economically producing an alloy, in which metallic elements each having a high melting point temperature do not remain not melted and the concentration of components are made unifrom, and which is not contaminated.

To attain the above-described object, the present invention provides a method for producing a high reactive alloy, comprising the steps of:
producing an alloy containing a metal having a high melting point temperature and Aℓ, a melting point temperature of said alloy being lowered to less than the melting point temperature of said metal;
crushing said alloy to form granules of alloy;
mixing said granules of alloy with metallic granules having a high melting point temperature, which has components other than components constituting said alloy, to make a mixture of said granules of alloy and said metallic granules;
pressing said mixture into a compact to form the compact; and
melting said compact by means of electron beams, Aℓ in said alloy being evaporated and an ingot being produced.

The present invention provides another method for producing a high reactive alloy, comprising the steps of:
producing an alloy containing a metal having a high melting point temperature and Aℓ, a melting point temperature of said alloy being lowered to less than the melting point temperature of said metal;
crushing said alloy to form granules of alloy;
mixing said granules of alloy with metallic granules having a high melting point temperature, which has components other than components constituting said alloy, to make a mixture of said granules of alloy and said metallic granules;
pressing said mixture into a compact to form the compact; and

premelting said compact, a first ingot being produced; and
melting said first ingot by means of electron beams , Aℓ in said alloy being evaporated and a second ingot being produced.

The present invention provides another method for producing a high reactive alloy, comprising the steps of:
producing an alloy containing a metal having a high melting point temperature and Aℓ, a melting point temperature of said alloy being lowered to less than the melting point temperature of said metal;
crushing said alloy to form granules of alloy;
mixing said granules of alloy with metallic granules having a high melting point temperature, which has components other than components constituting said alloy, to make a mixture of said granules of alloy and said metallic granules; and
melting said mixture by means of electron beams, Aℓ in said alloy being evaporated and an ingot being produced.

The present invention provides another method for producing a high reactive alloy, comprising the steps of:
producing an alloy containing a metal having a high melting point temperature and Aℓ from material ore, metallic granules, reducing agent and thermal booster and casting said alloy into a mold to form a first ingot; and
melting said ingot by means of electron beams, Aℓ in said alloy being evaporated and a second ingot being produced.

The present invention provides still another method for producing a high reactive alloy, comprising the steps of:
producing a metal having a high melting point temperature and Aℓ from material ore, first metallic granules, reducing agent and thermal booster and casting said metal into a mold to form a first ingot;
crushing said ingot to form granules of alloy;
mixing said granules of alloy with a second metallic granules to produce a mixture of said granules of alloy and said second metallic granules;
pressing said mixture into a compact and producing a compact; and
melting said compact as a consumable electrode by means of electron beams, Aℓ in said alloy being evaporated and a second ingot being produced.

The present invention provides yet another method for producing a high reactive alloy, comprising the steps of:
crushing ingots produced by means of the aforementioned methods;
mixing granules of said ingot with metallic granules as components of alloy and making a mixture of said granules of said ingot and said metallic granules;
pressing said mixture into a compact; and
melting said compact in a melting furance.

The above object and other objects and advantages of the present invention will become apparent from the detailed description which follows, taken in conjunction with the appended drawings.

Fig.1 is a schematic illustration showing an electron beam melting process of the present invention;

Fig.2 is a graphical representation indicating the relationship between the melting time and the alloy elements in the electron beam melting process of the present invention; and

Fig.3 is a schematic illustration showing a vacuum arc melting process of the present invention.

There are many technological difficulties in manufacture of an alloy of at least two sorts of metals having very different physical properties such as melting point temperatures, vapor pressures and the like. In the case of making an alloy of different metals each having a melting point temperature greatly different from each other, a metal having a high melting point temperature often remains not melted.

The following are generally carried out to produce a uniform ingot wherein metals do not remain not melted: A great amount of molten metal is charged into a crucible made of refractory. A feedstock is added to the molten metal. Said molten metal is sufficiently heated and left for a long time. Since the crucible made of refractory cannot be applied to the case of a high reactive alloy, a water-cooled copper vessel as a reaction vessel for converting metals to alloy is required to be used. However, since the volume of molten metal cannot be increased in the copper vessel, it is difficult to keep the great amount of molten metal, which is disadvatageous from the viewpoint of making an alloy.

A great difference of melting point temperatures generally means a great defference of vapor pressures. When plural metals each having a greatly different vapor pressure are melted under a vacuum, elements having a higher vapor pressure are preferentially evaporated, which makes it difficult to regulate components in the metals.

The present inventors payed attention to the fact that difficulties in conversion of high reactive metals to an alloy as mentioned above were caused by the difference of the melting point temperatures among metals. The Aℓ containing alloy whose melting point temperature is lowered by preliminarily converting the high reactive metals and Aℓ to an alloy is used. The difference of the melting point temperatures is large when a metal having a high melting temperature and a metal having a low melting temperature are used. However, when the Aℓ containing alloy whose melting point temperature is lowered by converting the high reactive metals and Aℓ to an alloy and the metal having a low melting point temperature are used, the difference of the melting point temperatures is decreased. Accordingly, when the Aℓ containing alloy is used, the difference of the melting point tempearatures is decreased, which makes it easy to produce an alloy. The reason for obtaining the feedstock by producing the alloy by adding Aℓ to a metal is that Aℓ can be easily evaporated and removed by means of the vacuum refining after the production of the alloy since the vapor pressure of Aℓ is comparatively high except that the effect of the low melting point temperature of the Aℓ can be expected. Further, since a vacuum degree in the electron beam melting furnace reaches 10^{-4} Torr, Aℓ can be easily evaporated and removed. The vacuum degree in melting furnaces other than the electron beam melting furnace is about 10^{-2} Torr even if a pressure in the melting furnaces is lower than the atmospheric pressure. The electron beam melting furnace is superior to the other melting furnaces in the evaporation and removal of Aℓ.

The lowest limit of the concentration of Aℓ in the Aℓ containing alloy is determined in consideration for the difference of the melting point temperatures between the Aℓ containing alloy and a mother phase metal. Since the highest limit of the melting point temperatures is determined by individual properties such as the melting rate of an alloy to be the object and the like, the highest limit cannot be unconditionally determined. However, the difference of the melting point temperatures between the above-mentioned alloy and the mother phase metal is desired to be about 600 °C or less. There is a tendency such that the larger the Aℓ content in the Aℓ containing alloy, the lower the melting point temperature of the Aℓ containing alloy. However, when the concentration of Aℓ is high, the amount of evaporating Aℓ is increased in the electron beam melting at the succesive step, which can interfere with a normal operation condition. Accordingly, the highest limit of the concentration of Aℓ is determined by the amount of evaporating Aℓ. The amount of evaporating Aℓ is determined by an equipment condition of the electron beam melting furnace.

An alloy of Aℓ and at least one sort of metal having a high melting point temperature is produced by means of an aluminium thermite reduction process at low cost. In this aluminium thermite reduction process, at least one sort of oxide of metal having a high melting point temperature is reduced by excessive Aℓ. The Aℓ content in the alloy is control led by regulating the amount of Aℓ. Besides the excessive Aℓ, an appropriate thermal booster is added to the alloy.

An alloy ingot produced by means of the aluminium thermite reduction process is used fundamentally as it is as a feedstock for the electron beam melting furnace at the successive step. To make the distribution of components in the alloy ingot uniform or to regulate the components in the alloy ingot, however, the alloy ingot can be premelted. The alloy ingot is melted in the melting furnace such as the vacuum arc melting furnace, plasma melting furnace or induction skull crucible melting furnace at atmospheric pressure or at a pressure of 10^{-2} Torr. The alloy ingot can be melted in the melting furnace of the inert atmosphere. During the premelting of the alloy ingot, pure Aℓ or metal having a high melting temperature can be added to the alloy ingot to regulate the components in the alloy ingot if necessary.

A high reactive metal of the object, which contains metals having high melting point temperatures, is produced by evaporating Aℓ in the Aℓ containing alloy in the electron beam melting furnace with the use of the Aℓ containing alloy obtained in such a manner as described above and the mother phase metal. When other constituent elements which are not contained in the above-mentioned Aℓ containing alloy are used as the feedstocks if necessary during the production of the high reactive alloy, a high reactive alloy of multiple components can be produced.

The high reactive alloy as described above is an alloy which cannot be melted, reacting with a refractory crucible made mainly of ordinary oxides in the molten state. The metals having high melting point temperatures are Ti, Nb, Mo, W, Sr, Ta, V and the like, and their melting point temperatures are 1650 °C or more.

Fig.1 is a vertical sectional view illustrating the electron beam melting furnace used in the method of the present invention. Fig.1 shows the case where all the amount of the feedstock used is a compact. In the drawing, reference numeral 1 denote an airtight vessel, 2 a compact, 5a and 5b electron guns. The ranges shown with dotted lines which are irradiated are various. Reference numeral 3 denotes a hearth which receives molten metal 8 produced by melting the above-mentioned compact and promotes the evaporation of Aℓ and conversion of metals into an alloy. Reference numeral 4 denotes a continuous casting mold, into which the above-mentioned molten metal is cast, and 9 a high reactive alloy produced.

The compact is successively melted by the electron beams 7a from the electron guns 5a and a molten metal flows into the hearth 3. The molten metal 8 in the hearth 3 is kept at a predetermined temperature by means of the electron guns 5a and 5b. During the whole time the molten metal 8 flows into the hearth 3 and flows out of the hearth 3 into the mold 4, Aℓ in the molten metal is evaporated and the conversion of the molten metal 8 to an alloy goes on. The aforementioned Aℓ is evaporated in the form of a pure Aℓ or a suboxide of Aℓ, for example, $A\ell_2O$, and discharged out of the airtight vessel 1.

The electron beams from the electron gun 5b keep the molten metal 8 at a predetermined temperature and prevent the molten metal 8 from being solidified by irradiating the upper portion of the mold and a portion at the vicinity of an outflow portion in the hearth 3, through which the molten metal 8 flows out. In this Preferred Embodiment, the mold 4 is a continuous casting mold. However, the mold is not limited to the aforementioned mold. An ordinary mold with the bottom can be used. The airtight vessel 1 is used to cause the atmosphere inside the electron beam melting furnace to be highly vacuous. A well-known vacuum device (not specifically shown) is used in this Preferred Embodiment. The vacuum degree is determined to be about 10^{-4} Torr. When the difference of the vapor pressures among the constiutent elements in molten metal 8 is large, the elements having high vapor pressures evaporate together with Aℓ, which decreases the yield of the elements. When the difference of the vapor pressures among the constiutent elements is large, the temperature of the molten metal produced by the electron beam melting or the melting time is controlled. The yield of the elements can be increased without excessively evaporating the elements by controlling the temperature or the melting time of the molten metal produced by the electron beam melting, by which the yield of the elements is stabilized

Fig.2 is a graphical representation designating the relationship between the melting time and the content of the components in the electron beam melting. The result obtained at the time when a Nb-45 wt.% Ti-10 wt.% Aℓ alloy was melted and the temperature of the molten alloy was kept at 2200 °C is shown. The abscissa denotes the time, during which the molten metal was kept as it was, and the ordinate the amount of Aℓ and Ti contained in the produced alloy. Fig.2 shows the result obtained by sampling the molten metal with the lapse of time in a batch melting in the test. In the case of the continuous melting, time on the ordinate corresponds to the melting rate.

As shown in Fig.2, initially, Aℓ is evaporated and the concentration of Aℓ is lowered under the condition of a predetermined melting temperature. After the concentration of Aℓ has decreased to zero, Ti begins to be evaporated. When the molten metal further continues to be irradiated by the electron beams, Ti is evaporated excessively. Accordingly, to obtain a Nb-Ti alloy having a predetermined concentration of the elements, it is good to stop melting at the moment when the concentration of Aℓ comes to zero, that is, at "A" point as shown in Fig. 2. The moment when the concentration of Aℓ reaches substantially zero is deterimined by the temperature of the molten metal and the melting time, that is, by the reaction time. When the melting is stopped before the concentration of Aℓ comes to zero, a Nb-Ti-Aℓ containing Aℓ can be obtained. In the case of the continuous operation as shown in Fig. 1, when the melting rate is deterimined, the melting time is determined. In consequence, the time corresponding to the above-mentioned "A" point can be determined by an operational experience.

As the electron beam melting process, besides the hearth melting process as shown in Fig. 1, a drip melting process can be used. In the hearth melting process as shown in Fig. 1, the hearth 3 is not arranged, but drops of the molten metal produced by melting the compact 2 by means of the electron guns 5 directly flow into the mold 9. In the hearth melting process, the components are easily regulated by charging components into the hearth 2, but the hearth 3 is required to be arranged and the power of the electron guns 5a and 5b is required to be increased. Conversely, in the drip melting process, the components are hard to regulate, but it is advantageous that an equipment cost is low. It can be determined in response to the purpose of melting which process is used. The above mentioned two melting processes are processes wherein a compact is used as a feedstock. It is unncessary, however, to use the compact, but crushed materials or granular materials can be directly added to the molten metal or directly charged into the hearth in the electron beam melting furnace. Further, to regulate the amount of evaporating Aℓ in the alloy produced in the electron beam melting furnace and the concentration of the components in the ingot, there are cases where the electron beam melting is carried out more than twice.

As the melting furnace for regulating the final components, the electron beam melting furnace, vacuum arc melting furnace, plasma melting furnace or induction skull crucible melting furance can be used. Those furnaces are furnaces, to which refractory as a material for a crucible is not applied, and in which the high reactive alloy can be produced smoothly.

When other alloy elements are simultaneously added to the alloy during production of the high reactive alloy by removing Aℓ in the alloy in the electron beam melting furnace, the high reactive alloy containing multiple components can be produced. Since the concentrations of many components are required to be regulated when the high reactive alloy of multiple components is produced, a separate melting step as the final step is desired to be arranged. The melting furance wherein the final components are regulated is desired to be a melting furance wherein refractory is not applied to the crucible. As the melting furance wherein the final components are regulated, the vacuum arc melting furnace, plasma melting furnace, induction skull crucible melting furnace, electron beam melting furnace or the like is pointed out.

In the case of producing a high reactive alloy which contains an alloy element having a high vapor pressure, since the above-mentioned alloy element having a high vapor pressure is quickly evaporated in an electron beam furnace of a high operational vacuum degree, it is difficult to regulate the components in the alloy. Accordingly, in this case, it is desired to evade the use of the electron beam melting furnace as the final step.

The difference of the melting point temperatures among the feedstocks at the final step is desired to be as small as possible. Since the melting point temperature of the high reactive alloy produced in this process is lowered compared with that of pure metal, the high reactive alloy is fit to use for a master alloy. Hereinafter, the master alloy is referred to as an alloy, which is produced in the electron beam melting furnace and which contains metals having high melting point temperatures.

Examples wherein the high reactive alloy containing Ti is produced by use of the master alloy, which contains metals having high melting point temperatures, as a feedstock will now be described below

The concentration of metal having a high melting point temperature in the master alloy is determined by how to set the melting point temperature of the master alloy. This is determined by a method of melting at the melting step wherein the master alloy is used as a material. For example, in the case of using a melting furnace wherein a high energy density is obtained as in the electron beam melting furnace or plasma melting furnace, the melting point temperature of the aforementioned master alloy can be higher than that in the case of using the vacuum arc melting furnace. In the case of using the electron beam melting furnace or plasma melting furnace, the melting point temperature of the aforementioned master alloy is desired to be 2300 °C or less. In the case of using the vacuum arc melting furance, the melting point temperature of the aforementioned master alloy is desired to be 2100 °C or less. To take a Ti-Mo master alloy for instance, in the cab of setting the melting point temperature of the master alloy for 2300 °C , the content of Mo is 70 wt.% at its maximum. In the case of setting the melting point temperature for 2100 °C , the content of Mo is 55 wt.% at its maximum.

A Ti alloy ingot is produced by using a master alloy as follows: The master alloy is crushed. Powder of the master alloy, a Ti source such as sponge Ti and other alloy elements are well mixed with each other. The mixture thereof is pressed into a compact and an consumable electrode is prepared. Melting processes are carried out more than twice in the vacuum arc melting furnace, and a Ti alloy ingot to be the object is produced.

Fig.3 is a schematic illustration showing a vacuum arc melting process of the present invention. The vacuum arc melting process is carried out in a vacuum, but an airtight vessel is omitted in Fig. 3. In the drawing, reference numeral 11 denotes a consumable electrode produced by pressing the sponge Ti, master alloy and other alloy elements into a compact. The consumable electrode 11 is melted from the bottom portion thereof by means of an arc 14, and molten metal produced in this way forms a pool 15 of the molten metal in a water-cooled copper mold 13. The surface of the pool 15 of the molten metal rises as the melting goes on, and the molten metal is successively solidified, by which a Ti alloy ingot 12 to be the object which has a high melting point temperature is produced.

Example 1

59 kg of granules of Nb-14 wt.% Aℓ alloy, which was produced by means of the aluminium thermite process and crushed, was well mixed with 10 kg of sponge titanium, and the mixture thereof was pressed into a compact 2 of 69 kg and 100 mm in diameter. The composition of the compact was Nb-12 wt.% Aℓ-14 wt.% Ti. The compact was melted under the condition of the power of the electron beam of 190 kW, the melting rate of 50 kg/Hr and the operational vacuum degree of 10^{-4} Torr, and Nb-15 wt.% Ti alloy of 59 kg and 136 mm in diameter was produced. When the power of the electron beam and the melting rate are greatly deviated from the above-mentioned power of the electron beam and melting rate, Ti is excessively evaporated and the yield of Ti is decreased.

Example 2

50 kg of granules of Nb-20 wt.% Aℓ alloy which was produced by means of the aluminium thermite process and crushed was well mixed with 37 kg of sponge titanium, and the mixture thereof was pressed into a compact 2 of 87 kg and 100 mm in diameter. The composition of the compact was Nb-43 wt.% T-11 wt.% Aℓ. The compact was melted under the condition of the power of the electron beam of 200 kW, the melting rate of 60 kg/Hr and the operational vacuum degree of 10^{-4} Torr, and Nb-47 wt.% Ti alloy of 75 kg and 136

mm in diameter was produced.

Example 3

53 kg of granules of Nb-20 wt.% Aℓ alloy produced by means of the aluminium thermite process was well mixed with 40 kg of sponge titanium, and the mixture thereof was pressed into a compact of 93 kg and 100 mm in diameter. An ingot of Nb-43 wt.% Ti-11wt.% Aℓ alloy was produced by melting the compact in the vacuum arc melting furnace. The ingot was melted under the condition of the power of the electron beam of 200 kW/Hr, the melting rate of 40 kg/Hr and the operational vacuum degree of 10^{-4} Torr. An ingot of Nb-46 wt.% Ti alloy of 72 kg and 136 mm in diameter was produced. This Nb-Ti ingot was remelted in the plasma hearth melting furance to regulate the components in this alloy , and an Nb-47 wt.% Ti alloy of 74 kg was produced by adding 1.8 kg of Ti to the Nb-Ti alloy.

Example 4

53 kg of granules of Nb-20 wt.% Aℓ alloy produced by means of the aluminium thermite process was well mixed with 42 kg of sponge titanium, and the mixture thereof was pressed into a compact of 95 kg and 100 mm in diameter. The compact was melted under the condition of the power of the electron beam of 180 kW, the melting rate of 50 kg/Hr and the operational vacuum degree of 10^{-4} Torr. An ingot of Nb-46 wt.% Ti-6 wt.% Aℓ of 90 kg and 136 mm in diameter was produced. This ingot was melted under the condition of the power of the electron beam of 190 kW, the melting rate of 60 kg/Hr and the operational vacuum degree of 10^{-4} Torr, and an ingot of an Nb-49 wt.% Ti alloy of 83 kg and 136 mm in diameter was produced.

Example 5

The compact was used as the feedstock in the Examples 1 to 4, but granular melting materials were used in this Example 5. 50 kg of granular Nb-20 wt.% Aℓ produced by means of the aluminium thermite process was well mixed with 37 kg of scrap titanium to make the feedstock. This feedstock was charged into a hearth from a material feeder (not shown in Fig.1). The feedstock was melted under the condition of the power of the electron beam of 200 kW, the melting rate of 60 kg/Hr and the operational vacuum degree of 10^{-4} Torr. An ingot of Nb-47 wt.% Ti alloy of 75 kg and 136 mm in diameter was produced.

Example 6

64 kg of Nb ore, 51 kg of sponge titanium and 25 kg of powdery aluminium together with thermal booster were mixed with each other, and the mixture thereof was melted by means of the aluminium thermite process, by which a Nb-Ti-Aℓ alloy of 87 kg was produced. This alloy was cast into a mold of 100 mm in diameter, and a compact was obtained. The composition of the alloy on this occasion was Nb-43 wt.% Ti-11 wt.% Aℓ. This compact was melted under the condition of the power of the electron beam of 200 kW, the melting rate of 60 kg/Hr and the operational vacuum degree of 10^{-4} Torr, by which an ingot of Nb-47 wt.% Ti alloy of 75 kg and 136 mm in diameter was produced.

Example 7

65 kg of Nb ore, 95 kg of Ti ore (rutile) and 69 kg of powdery aluminium together with thermal booster were mixed with each other, and the mixture thereof was melted by means of the aluminium thermite process, by which a Nb-Ti-Aℓ alloy of 87 kg was produced. This alloy was cast into a mold of 100 mm in diameter to make a compact. The composition of the alloy on this occasion was Nb-43 wt.% Ti -11 wt.% Aℓ. The compact was melted under the condition of the power of the electron beam of 200 kW, the melting rate of 60 kg/Hr and the operational vacuum degree of 10^{-4} Torr, by which an ingot of Nb-47 wt.% Ti alloy of 75 kg and 136 mm in diameter was produced.

Example 8

64 kg of Nb ore, 18 kg of Ti ore (rutile) 40 kg of sponge titanium and 34 kg of powdery aluminium together with thermal booster were mixed with each other , and the mixture thereof was melted by means of the aluminium thermite process, by which a Nb-Ti-Aℓ alloy of 87 kg was produced. This alloy was cast into a mold of 100 mm in diameter to make a compact 2. The composition of the alloy on this occasion was Nb-43 wt.%Ti-11 wt.% Aℓ. The compact was melted under the condition of the power of the electron beam of 200 kW, the melting rate of 60 kg and the operational vacuum degree of 10^{-4} Torr, by which an ingot of Nb-46 wt.% Ti alloy of 75kg and 136 mm in diameter was produced.

Example 9

63 kg of Nb ore, 64 kg of sponge titanium and 55 kg of powdery aluminium together with thermal booster were mixed, and the mixture thereof was melted by means of the aluminium thermite process, by which a Nb-Ti-Aℓ alloy of 75 kg was produced. This alloy was cast into a mold of 100

mm in diameter. The composition of the alloy on this occasion was Nb-31 wt.% Ti-14 wt.% Aℓ. The alloy was crushed, and the crushed alloy was well mixed with 15 kg of sponge titanium. The mixuture thereof was melted and an alloy obtained was pressed into a consumable electrode of Nb-43 wt.% Ti-11 wt.% Aℓ of 86 kg. This consumable electode as the compact was melted under the condition of the power of the electron beam of 200 kW, the melting rate of 60 kg/Hr and the operationalloy vacuum degree of 10^{-4} Torr, by which an ingot of Nb-47 wt.% Ti alloy of 75 kg and 136 mm in diameter was produced.

Example 10

83 kg of Nb-33 wt.% Ta-25 wt.% Aℓ alloy produced by means of the aluminium thermite process was well mixed with 66 kg of sponge titanium, and the mixture thereof was pressed into a compact of 149 kg and 100 mm in diameter. The composition of the compact was Nb-18 wt.% Ta-44 wt.% Ti-14 wt.% Aℓ. The compact was twice melted in the electron beam melting furnace under the condition of the power of the electron beam of 230 kW, the melting rate of 40 kg/Hr and the operational vacuum degree of 10^{-4} Torr, and Aℓ was evaporated and removed from the alloy, by which an ingot of Nb-43 wt.% Ti-25 wt.% Ta alloy of 102kg and 136 mm in diameter was produced.

Example 11

7 kg of W-30 wt.% Aℓ alloy produced by means of the aluminium thermite process and 51 kg of pure Ta were pressed into a compact to be used as a feedstock. The composition of the alloy on this occasion was Ta-9 wt. %-3 wt.% Aℓ. The compact was melted under the condition of the power of the electron beam of 200 kW, the melting rate of 30 kg/Hr and the operational vacuum degree of 10^{-4} Torr, and Aℓ was evaporated and removed from the alloy, by which an ingot of Ta-10 wt.% W alloy of 53 kg was produced.

Example 12

59 kg of Nb-14 wt.% Aℓ alloy produced by means of the aluminium thermite process was well mixed with 12 kg of sponge titanium, and the mixture thereof was pressed into a compact of 71 kg and 100 mm in diameter. The composition of the compact was Nb-12 wt.% Aℓ-17 wt.% Zr. The compact was melted under the condition of the power of the electron beam of 190 kW, the melting rate of 50 kg/Hr and the operational vacuum degree of 10^{-4} Torr, by which an ingot of Nb-15 wt.% Zr alloy of 59 kg and 136 mm in diameter was produced.

Example 13

To produce an ingot of Ti-11.5 wt.% Mo-6 wt.% Zr-4.5 wt.% Sn alloy, the following melting process was adopted. 50 kg of granular Mo-20 wt.% Aℓ produced by means of the aluminium thermite process was well mixed with 96 kg of sponge titanium, and the mixture thereof was pressed into a compact. The melting point temperature of Mo-20 wt.% Aℓ alloy was about 1900 °C. The composition of the compact on this occasion was Ti-27 wt.% Mo-7 wt.% Aℓ. The alloy as the compact 2 was melted by means of the hearth melting process in the electron beam melting furance, and Aℓ was evaporated and removed from the alloy, by which an ingot of Ti-29 wt.% Mo alloy of 200 mm in diameter was produced. The melting point of the Ti-29 wt.% Mo alloy was about 1900 °C. This master alloy ingot was crushed and granulated. The particle size of the granulated alloy was made uniform.

Subsequently, 53 kg of sponge titanium, 42 kg of the master alloy (Ti-29 wt.% Mo) 6 kg of sponge zirconium and 5 kg of granular Sn were well mixed with each other, and the mixture thereof was pressed into a compact. Thereafter, an electrode was produced from the compact. An ingot of 95 kg and 200 mm in diameter was produced by melting twice the electrode in a VAR furnace. It was confirmed that Mo did not remain not melted and did not precipitate.

Example 14

To produce an ingot of Ti-15 Mo-5 Zr-3 Aℓ alloy, the following melting process was adopted. 57 kg of granular Mo-20 wt.% Aℓ alloy produced by means of the aluminium thermite process was well mixed with 82 kg of sponge Ti, and the mixture thereof was pressed into a compact. The melting point temperature of the Mo-20 wt.% Aℓ alloy was about 1900 °C. The composition of the compact on this occasion was Ti-33 wt.% Mo-8 wt.% Aℓ. The compact was melted in the electron beam melting furance (the drip melting process), and Aℓ was evaporated and removed, by which an ingot of Ti-33 wt.% Mo-7wt.% Aℓ alloy was produced. This master alloy ingot was crushed and the crushed ingot was granulated. The particle size of the granulated alloy was made uniform.

Subsequently, 53 kg of sponge Ti, 47 kg of the master alloy (Ti-33 wt.% Mo-7 wt.% Aℓ) and 5 kg of sponge Zr were well mixed with each other, and the mixture thereof was pressed into a compact. Thereafter, an electrode was produced from the compact. An ingot of 95 kg and 200 mm in diameter was produced by melting twice the electrode in a VAR furance.

Example 15

To produce an ingot of Ti-10 V-10 Mo alloy, the following melting process was adopted. 61 kg of granular V-5 wt.% Aℓ alloy (the melting point temperature was about 1850 °C) produced by means of the aluminium thermite process was well mixed with 73 kg of sponge Ti, and the mixture thereof was pressed into a compact. The composition of the compact on this occasion was Ti-43 wt.% V-2 wt.% Aℓ. An ingot of Ti-46 wt.% V alloy (t melting point temperature was about 1650°C) of 200 mm in diameter was produced by melting the compact in the electron beam melting furnace, evaporating and removing Aℓ. 51 kg of granular Mo-20 wt.% Aℓ alloy (the melting point temperature was about 1900°C) produced by means of the aluminium thermite process was well mixed with 95 kg of sponge Ti, and the mixture thereof was pressed into a compact. The composition of the compact on this occasion was Ti-28 wt.% Mo-7 wt.% Aℓ. An ingot of Ti-30 wt.% Mo alloy (the melting point was about 1900°C) of 200 mm in diameter was produced by melting the compact in the electron beam melting furnace (the. hearth melting process) and evaporating and removing Aℓ. The aforementioned two master alloy ingots were crushed and granulated. The particle size of the granulated alloy was made uniform. Subsequently, 47 kg of sponge Ti and the master alloys (23 kg of Ti-46 wt.% V alloy and 35 kg of Ti-30 wt.% Mo alloy) were well mixed with each other, and the mixture thereof was pressed into a compact. Then, an electrode was produced from the compact. An ingot of 95 kg and 200 mm in diameter was produced by melting twice the electrode in the vacuum melting furnace.

Example 16

To produce an ingot of Ti-10V-10Mo alloy, the following melting process was adopted. 24 kg of granular V-5 wt.% alloy (the melting point temperature was about 1850°C) produced by means of the aluminium thermite melting process, 28 kg of granular Mo-20 wt.% Aℓ alloy (the melting point temperature was about 1900 °C) and 80 kg of sponge Ti were well mixed with each other, and the mixture thereof was pressed into a compact. The composition of the compact on this occasion was Ti-17 wt.% V-17 wt.% Mo-5 wt.% Aℓ. An ingot of Ti-18 wt.% V-18 wt.% Mo alloy of 125 kg and 200 mm in diameter was produced by melting the compact in the electron beam melting furnace and evaporating and removing Aℓ. This master alloy was crushed and the crushed master alloy was granulated. The particle size of the granulated alloy was made uniform.

Next, 47 kg of sponge Ti was well mixed with 58 kg of the master alloy (Ti-18 wt.% V-18 wt.% Mo), the mixture thereof was pressed into a compact. Thereafter, an electrode was produced. An ingot of 95 kg and 200 mm in diameter was produced by melting twice the electrode in the vacuum arc melting furnace.

Claims

1. A method for producing a high reactive alloy, characterized by comprising the steps of:
producing an alloy containing a metal having a high melting point temperature and Aℓ, a melting point temperature of said alloy being lowered to less than the melting point temperature of said metal;
crushing said alloy to form granules of said alloy;
mixing said granules of alloy with metallic granules having a high melting point temperature, which has components other than components constituting said alloy, to make a mixture of said granules and said metallic granules;
pressing said mixture into a compact to form the compact; and
melting said compact by means of electron beams, Aℓ in said alloy being evaporated and an ingot being produced.

2. The method of claim 1, characterized in that
said metal having a high melting point temperature is Nb;
said metallic granules having a high melting point temperature is of sponge titanium; and
said ingot is of Nb-Ti alloy.

3. The method of claim 1, characterized in that
said metal having a high melting point temperature is Nb and Ta;
said metallic granules having a high melting point temperature is of sponge titanium; and
said ingot is of Nb-Ti-Ta alloy.

4. The method of claim 1, characterized in that
said metal having a high melting point temperature is W;
said metallic granules having a high melting point powder is of pure Ta; and
said ingot is of Ta-W alloy.

5. The method of claim 1, characterized in that
said metal having a high melting point temperature is Nb;
said metallic granules having a high melting point temperature is of sponge zirconium; and
said ingot is of Nb-Zr alloy.

6. The method of claim 1, characterized in that
said metal having a high melting point temperature is Mo;

said metallic granules having a high melting point temperature is of sponge titanium; and
said ingot is of Ti-Mo alloy.

7. The method of claim 1, characterized in that
said metal having a high melting point temperature is V;
said metallic granules having a high melting point temperature is of sponge titanium; and
said ingot is of Ti-V alloy.

8. A method for producing a high reactive alloy, characterized by comprising the steps of:
producing an alloy containing a metal having a high melting point temperature and Aℓ, a melting point temperature of said alloy being lowered to less than the melting point temperature of said metal;
crushing said alloy to form granules of said alloy;
mixing said granules with metallic granules having a high melting point temperature, which has components other than components constituting said alloy, to make a mixture of said granules and said metallic granules:
pressing said mixture into a compact to form the compact;
premelting said compact, a first ingot being produced; and
melting said first ingot by means of electron beams, Aℓ in said alloy being evaporated and a second ingot being produced.

9. The method of claim 8, characterized in that said compact is premelted in a vacuum induction melting furnace.

10. The method of claim 8, characterized in that said compact is premelted in a vacuum arc melting furnace.

11. The method of claim 8, characterized in that said compact is premelted in a plasma melting furnace.

12. The method of claim 8, characterized in that said compact is premelted in an induction skull crucible melting furnace.

13. The method of claim 8, characterized by further comprising the step of remelting said high reactive alloy in a melting furnace.

14. The method of claim 13, characterized in that said melting furnace includes an electron beam melting furnace, vacuum arc melting furnace, plasma melting furnace and induction skull crucible melting furnace.

15. The method of claim 8, characterized in that
said metal having a high melting point temperature is Nb;
said metallic granules having a high melting point temperature is of sponge titanium; and
said second ingot is of Nb-Ti alloy.

16. A method for producing a high reactive alloy, charcterized by comprising the steps of:
producing an alloy containing a metal having a high melting point temperature and Aℓ, a melting point temperature of said alloy being lowered to less than the melting point temperature of said metal;
crushing said alloy to form granules of alloy;
mixing said granules of alloy with metallic granules having a high melting point temperature, which has components other than components constituting said alloy, to make a mixture of said granules and said metallic granules; and
melting said mixture by means of electron beams, Aℓ in said alloy being evaporated and an ingot being produced.

17. The method of claim 16, characterized in that
said metal having a high melting point temperature is Nb;
said metallic granules having a high metling point temperature is of scrap titanium; and
said ingot is of Nb-Ti alloy.

18. A method for producing a high reactive alloy, characterized by comprising the steps of:
producing an alloy containing a metal having a high melting point temperature and Aℓ from material ore, powder of metal, reducing agent and thermal booster and casting said alloy into a mold to form a first ingot; and
melting said ingot by means of electron beams, Aℓ in said alloy being evaporated and a second ingot being produced.

19. The method of claims 1, 8, 16 and 18, characterized in that said alloy or metal has a melting point temperature of 1650° C or more.

20. The method of claim 18, characterized in that
said material ore is Nb ore;
said powder of metal is of sponge titanium; and
said reducing agent is powdery aluminium.

21. The method of claim 18, characterized in that
said material ore is Nb ore and Ti ore; and
said reducing agent is powdery aluminium.

22. A method for producing a high reactive alloy, characterized by comprising the steps of:
producing a metal having a high melting point temperature and Aℓ from material ore, a first metallic granules, reducing agent and thermal booster and casting said metal into a mold to form a first ingot;
crushing said ingot to form granules of said alloy;
mixing said granules of alloy with a second metallic granules to produce a mixture of said granules of alloy and said second metallic granules;
pressing said mixture into a compact and producing a compact; and
melting said compact as a consumable electrode by means of electron beams, Aℓ in said alloy being evaporated and a second ingot being produced.

23. The method of claim 22, characterized in that said metal has a melting point temperature of 1650 ° C or less.

24. The method of claims 1, 8, 16, 18 and 22,

characterized in that said metal is at least one selected from the group consisting of Ti, Nb, Mo, W, Zr, Ta and V.

25. The method of claims 1, 18 and 22, characterized in that said alloy is produced by means of the aluminium thermite process.

26. The method of claim 22, characterized in that said material ore is Nb ore;
said first and second metallic granules are of sponge titanium; and
said reducing agent is of powdery aluminium.

27. A method for producing a high reactive alloy, characterized by comprising the steps of:
crushing ingots produced by means of the methods of claims 1, 8, 16, 18 and 22;
mixing granules of said ingot with metallic granules as components of alloy to form a mixture of said granules of said ingot and said metallic granules;
pressing said mixture into a compact; and
melting said compact in a melting furance.

28. The method of claim 27, characterized in that said melting furance includes an electron beam melting furnace, vacuum arc melting furnace, plasma melting furance and induction skull crucible furance.

FIG.1

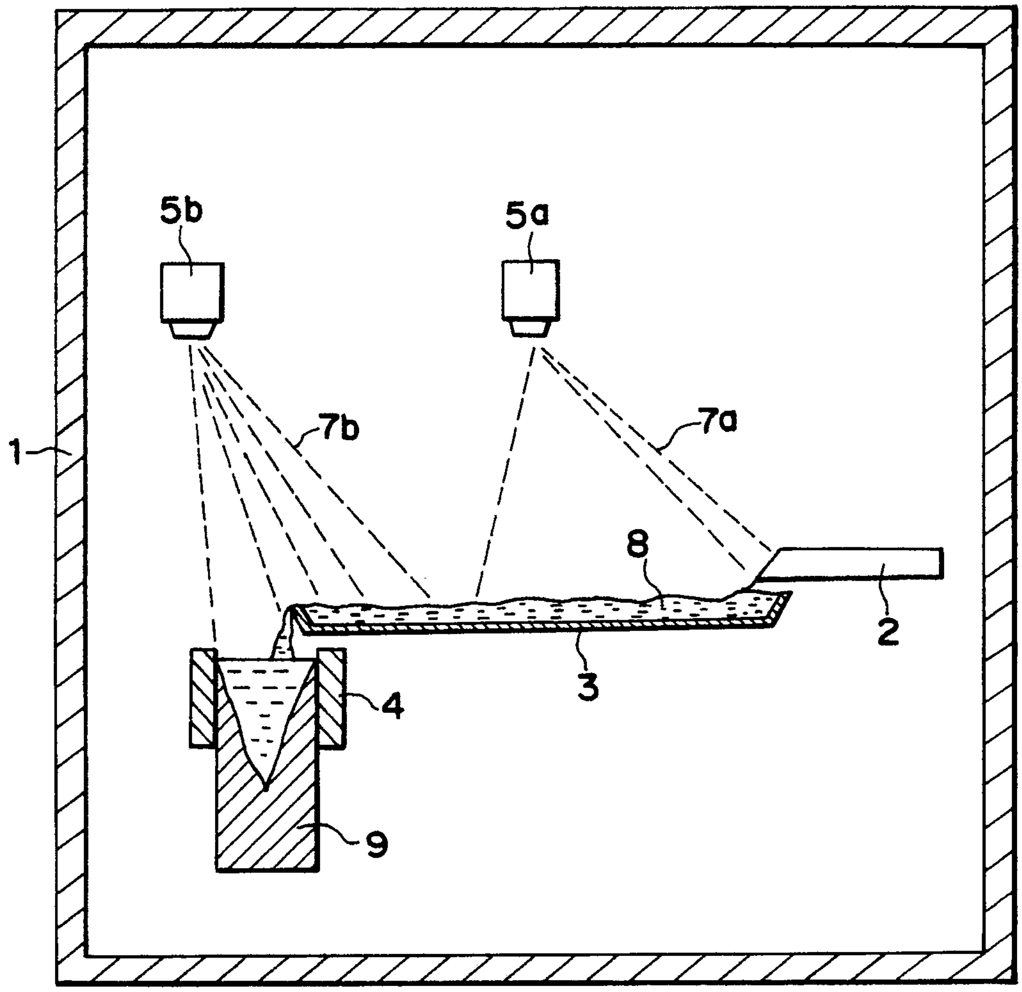


FIG. 2

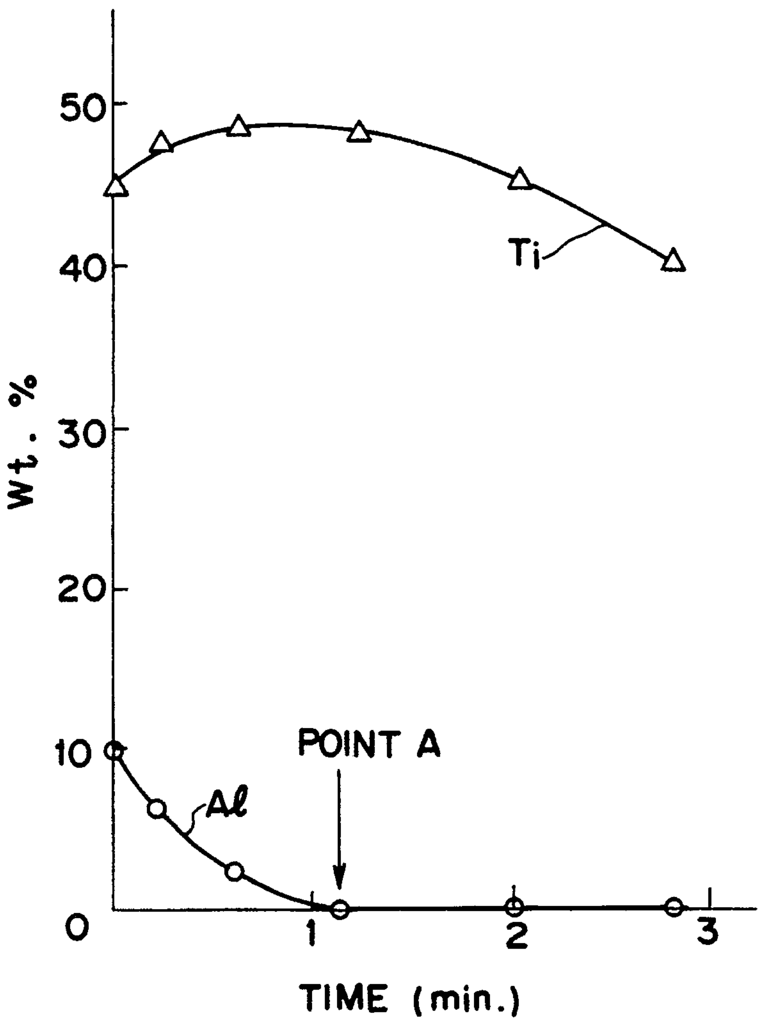
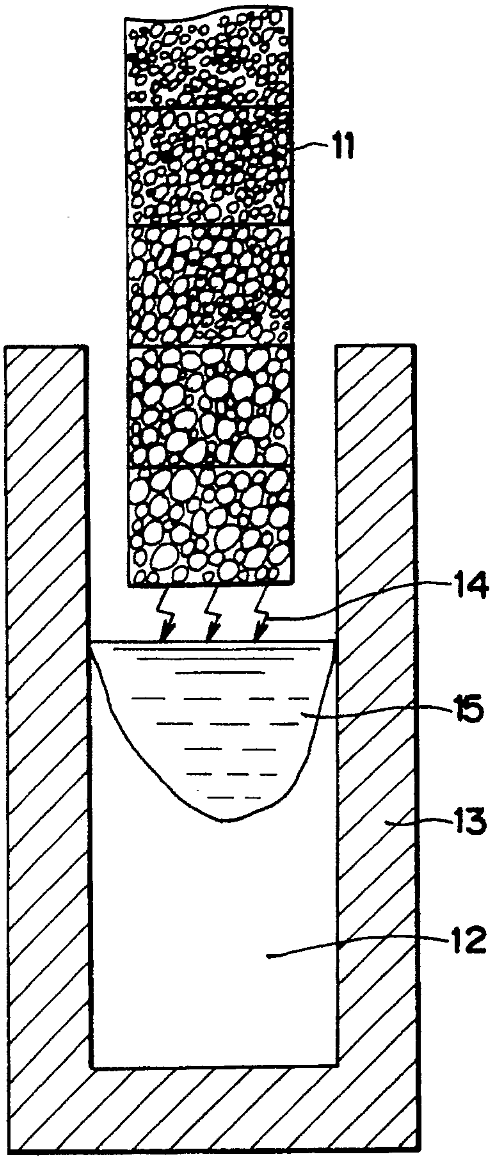


FIG. 3



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EUROPEAN SEARCH REPORT

Application Number

EP 90 12 1960

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.5)
Y	EP-A-0 073 585 (SPECIAL METALS CORP.) * Claims 1-3,5,7,8,12,13,15 * – – –	1	C 22 C 1/02 C 22 B 9/22
Y	FR-A-2 231 768 (ZABORONOK et al.) * Claims 1,2 * – – –	1	
A	FR-A-1 458 238 (CEA) * Abstract points 1,3,6,7 * – – –	1,8,16,22, 27	
A	US-A-3 342 250 (TREPPSCHUH et al.) * Claims 1-9; figures 1,3 * & FR-A-1 411 991 * – – –	1,8	
A	EP-A-0 259 856 (NIPPON KOKAN K.K.) * Claims 1-11 * – – –	1,27	
A	GB-A-2 160 224 (TOHO TITANIUM CO.) * Claims 11-20 * & JP-A-85 251 235 (Cat. A,D) – – –	1,8,16,18, 22,27	
A	US-A-3 700 428 (ANVAR) * Claims 1-8 * – – – – –	1,8,16,22, 27	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 22 C 1/02 C 22 B 9/22 B 22 D 11/10

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	28 February 91	LIPPENS M.H.

CATEGORY OF CITED DOCUMENTS

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