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A request for correction for changing "boron nitrate" into "boron nitride" on claims 6 & 14 and on page 4, line 7 has been filed pursuant to Rule 88 EPC. A decision on the request will be taken during the proceedings before the Examining Division (Guidelines for Examination in the EPO, A-V, 3.).

(54) **Method and system for continuously casting copper alloys**

(57) This invention is related to a method and a system for continuously cast copper alloys with high affinity for carbon, where the casting die is at least partly made of, or at least partly covered with, material resistant to

copper alloy to be cast and the flux cover is made of material resistant to copper alloy to be cast.

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Description

FIELD OF INVENTION

[0001] This invention relates to method and system for continuously casting copper alloys. More specifically it relates to method and system advantageous with alloys having high affinity for carbon.

BACKGROUND OF THE INVENTION

[0002] It is common to use continuous casting in vertical, horizontal and down casting. Many prior art documents are related to this field of casting technology. These prior art documents are for example US 2 553 921 and WO 02/20194 A1. In upward casting process the profiled metal products are continuously cast by maintaining a water-cooled nozzle immersed into a melt to receive and cool the melt. The nozzle is immersed so deep into the melt that the point of solidification of the received melt is below the surface level of the outside melt and the solidified melt is then pulled upwards while being further cooled.

[0003] The continuous casting is demanding high requirements for casting dies and casting environment. For these requirements not all alloys are suitable for continuous casting with prior art methods and systems. For example the casting of CuCr, CuCrZr, CuZr or CuTi alloys has mainly been limited in production to billet casting. For the purpose of describing this technology the term "continuous casting" is used for describing casting strips or wires with thickness/diameter of maximum 50 mm for coldworking the material further in the process. In certain circumstances continuous casting of CuCr may be possible but at low ppm levels Cr (<2500 ppm).

[0004] The limitation to continuously casting these alloys (CuCr, CuCrZr and CuZr) is due their high affinity for carbon. The typical die for continuous casting of copper and copper alloys is made of graphite, which undergoes a reduction reaction with Cr and Zr to form carbides. Graphite melt covers are also common and undergo same reactions as the casting die. During casting the Cr and Zr attacks the die surface until casting is stopped due any of the following reasons: surface defects, separation of the rod at the liquidus interface, tapering of the die due to reactions with Cr and Zr causing the cast material to become lodged in the die area, etc.

SUMMARY OF THE INVENTION

[0005] The objects of the invention are to overcome previously described problems and achieve method and systems enabling the continuous casting of copper alloys with high affinity for carbon.

[0006] These objects are achieved with material selection for the casting die and the protection of the melt. To continuously cast the copper alloys with the high affinity for carbon the prior art die material is replaced with

a ceramic, special ceramic, stabilized ceramic, ceramic composite or other non reactive material and the prior art type flux cover is changed.

[0007] These above mentioned objects are achieved by a method and a system described later in the independent claims. In the dependent claims are presented other advantageous embodiments of the invention.

[0008] The developed new method and system for continuously casting copper alloys having high affinity for carbon may be used in vertical, horizontal and down casting.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0009] In the following the preferred embodiments of the invention are described in more details with some examples of suitable materials.

[0010] To continuously cast copper alloys with high affinity for carbon it has been found necessary to replace the die material at least partly with a material that is less inactive as graphite die. Other possibility is to coat the die with sufficient material. Such materials are ceramics, special ceramics, stabilized ceramics, ceramic composites or other non-reactive materials. Such alloys that have high affinity for carbon are for example CuCr, CuCrZr, CuZr or CuTi alloys, but the method and the system are not limited to only these examples. They can be used with any alloys that have high affinity for carbon. The prior art use of graphite dies, which were exposed to Cr and Zr was leading to short life of the dies. The die is not the only source of carbon and therefore we have to use also an alternative flux cover. Chromium corrodes graphite die through carbide reaction $\text{Cr} + \text{C} \rightarrow \text{Cr}_3\text{C}_2$ and then the rough die surface mechanically tears the thin solidified skin of the rod. This happens at the point where the cooled metal melt is beginning to solidify inside the casting die. The phenomenon is resulting to poor quality of the product.

[0011] The idea of the invention is to prevent the above-mentioned reaction by changing the die and flux cover material to more resistant one. The materials that were found advantageous for the purpose and resistant to Cr are for example nitrides or oxides, ceramic composite materials or stabilized composites. Also special ceramic materials $\text{M}_{n+1}\text{AX}_n$, where M is an early transition metal, A is an element from the A groups usually IIIA or IVA, X is either nitrogen or carbon and n is 1, 2 or 3, are suitable. These are called 3one2 materials and are divided into three groups based on the number of atoms of the M, A and X elements in each molecule. These groups are known as 211, 312 and 413 materials. To date more than 50 so called MAX phases are known. Few examples of these materials are Ti_2AlN , Cr_2GaN and Ti_3SiC_2 . The die can be made of these said materials or be just coated with them. The coating can be done for example with using PVD (Physical Vapor Deposition coating), CVD (Chemical Vapor Deposition

coating) methods or any other known method suitable for coating.

[0012] In most cases the thermal conductivity of graphite is three to thirty times greater than the thermal conductivity of ceramic, ceramic composite, special ceramic or stabilized ceramic. This fact enables to control the solidification point of the melt inside the casting die more accurately. This is very critical for the quality of the final product.

[0013] The suitable ceramics are for example boron nitrate (BN), boron nitrate doped with zirconium oxide (BN+ZrO₂), zirconium oxide (ZrO₂), and doped zirconium oxides (ZrO₂Me, where Me = Ba, Ca or Sr). These materials available at the time are found to provide best solutions to the problem. Also aluminum nitride (AlN) has been found to be an alternative die material due its low wetting angle with copper alloys. From the Ellingham diagrams can be seen that the above-mentioned materials have superior properties over the graphite when working in a Cr and/or Zr enriched environment. Also other suitable ceramics, stabilized ceramics (e.g. yttrium stabilized zirconium or magnesium partially stabilized zirconium) or ceramic composite materials that are not precisely mentioned here can be used.

[0014] For vertical or horizontal casting of the rod the die may be composed entirely of selected ceramic, stabilized ceramic, ceramic composite or other suitable material. In special occasions the die may be constructed so that the selected material is only an insert into the casting die. For down or horizontal casting the die may be composed again entirely of the selected material and in some cases it may be constructed of sheets or stacked laminations of the selected material.

[0015] Ceramics suitable for at least for coating are for example nitrides or oxides such as TiN, ZrN, Al₂O₃ or Cr₂O₃. These are just examples of the materials suitable for the purpose and the materials are not in any way limited to just these. The main idea is to produce a die that reacts as little as possible with the melt.

[0016] For protecting the melt it has been found that the most effective melt fluxes for casting CuCr, CuCrZr and CuZr are the chloride based salts. For example BaCl₂, CaCl₂ and SrCl₂ can be used. They have melting points 962°C, 772°C and 874°C respectively and exist as liquids below and above the melting point of copper. Another feature that is important along with the melting point and chemical reactivity in the use of the chlorides above is the compatibility of the decomposition product from the chloride, i.e. BaO, CaO and SrO. Melting point of the binary chloride-oxide system must be below the casting temperature in order to assure a complete coverage of the alloy surface by the molten flux.

[0017] For example from the phase diagrams can be seen that all the chlorides (MeCl₂, where the Me = Ba, Ca or Sr) can dissolve 20-50 mol% the corresponding oxide (MeO) at 1200°C. CaCl₂ is probably the most sensitive among the selected substances, as its ability to dissolve the oxide is the smallest, but still substantial,

larger than 20 mol%.

[0018] Based on the vapor pressure estimations BaCl₂ and SrCl₂ are preferred to CaCl₂ as their vapor pressures are somewhat smaller than that of CaCl₂. At 1200°C vapor pressures of BaCl₂ and SrCl₂ are about 10^{-3.4} bar whereas that of CaCl₂ is about 10⁻³ bar. Thus vaporization losses of BaCl₂ and SrCl₂ should therefore be slightly less intensive.

[0019] While the invention has been described with reference to its preferred embodiments, it is to be understood that modifications and variations will occur to those skilled in the art. Such modifications and variations are intended to fall within the scope of the appended claims.

Claims

1. Method for casting copper alloys with high affinity for carbon, comprising the steps of:
 - selecting the die material resistant to copper alloy to be cast; and
 - selecting the flux cover material resistant to copper alloy to be cast.
2. Method according to claim 1, wherein the coating of the die is done at least partly with said material resistant to copper alloy to be cast.
3. Method according to claim 1, wherein the coating of the die is done to whole die with said material resistant to copper alloy to be cast.
4. Method according to claim 1, wherein the die is at least partly made of the material resistant to copper alloy to be cast.
5. Method according to claim 1, wherein the whole die is made of the material resistant to copper alloy to be cast.
6. Method according to any of claims 1 to 5, wherein selecting the die material is done from ceramics, such as boron nitrate (BN), boron nitrate doped with zirconium oxide (BN+ZrO₂), zirconium oxide (ZrO₂), and doped zirconium oxides (ZrO₂Me) or like.
7. Method according to any of claims 1 to 5, wherein selecting the die material is done from special 3one2 ceramic materials M_{n+1}+AX_n, where M is an early transition metal, A is an element from the A groups usually IIIA or IVA, X is either nitrogen or carbon and n is 1, 2 or 3.
8. Method according to any of claims 1 to 5, wherein selecting the die material is done from stabilized ceramics, such as yttrium stabilized zirconium, magnesium partially stabilized zirconium or like.

9. Method according to any of claims 1 to 5, wherein the die material is aluminum nitride (AlN).
10. Method according to any of claims 1 to 5, wherein the die material is ceramic composite. 5
11. Method according to claim 1, wherein selecting the flux cover material is done among chloride based salts such as BaCl₂, CaCl₂, SrCl₂ or like. 10
12. A system for continuously cast copper alloys with high affinity for carbon, where the casting die is at least partly made of, or at least partly covered with, material resistant to copper alloy to be cast and the flux cover is made of material resistant to copper alloy to be cast. 15
13. A system according to claim 12, wherein the casting die material is selected from ceramics, special 3one2 ceramics, ceramic composites, stabilized composites or aluminum nitride (AlN). 20
14. A system according to claim 13, wherein the ceramics are boron nitrate (BN), boron nitrate doped with zirconium oxide (BN+ZrO₂), zirconium oxide (ZrO₂), and doped zirconium oxides (ZrO₂Me) or like. 25
15. A system according to claim 13, wherein the special 3one 2 ceramics are materials M_{n+1}+AX_n, where M is an early transition metal, A is an element from the A groups usually IIIA or IVA, X is either nitrogen or carbon and n is 1, 2 or 3. 30
16. A system according to claim 13, wherein the stabilized composites are yttrium stabilized zirconium, magnesium partially stabilized zirconium or like. 35
17. A system according to claim 12, wherein the flux cover material is chloride based salt such as BaCl₂, CaCl₂, SrCl₂ or like. 40

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