



(1) Publication number:

0 444 394 A2

(12)

# **EUROPEAN PATENT APPLICATION**

21) Application number: 91100015.6

(51) Int. Cl.5: C23C 4/10

2 Date of filing: 02.01.91

30 Priority: 29.01.90 JP 16153/90

Date of publication of application:04.09.91 Bulletin 91/36

② Designated Contracting States:
CH DE FR GB IT LI

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- 64) Ceramic spray coating material.

© A ceramic spray coating material comprising zirconia and yttria, wherein the purity of a mixture of zirconia and yttria is 99,6% by weight or more is described.

This ceramic spray-coating material has an excellent bonding force, as compared to the prior art material.

#### **CERAMIC SPRAY COATING MATERIAL**

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Background of the invention

Field of the invention

The present invention relates to a ceramic spray coating material comprising zirconia and yttria.

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Description of the prior art

There is a continuous casting mold conventional known from Japanese Patent Publication No. 86/005819, which has a Ni-plating layer formed on an inner surface and a Co-Mo-Cr alloy layer spray-coated thereon and comprising of 45 to 65 % by weight of Co, 20 to 40 % by weight of Mo and the balance of Cr. If such continuous casting mold is used as a casting mold for usual discontinuous casting processes, e.g., a low pressure casting or gravity casting process, a disadvantage is encountered: A gas cannot be sufficiently eliminated during casting and hence, a blow (ruggedness) may be produced, resulting in an inferior surface profile of a molded product.

For the purpose of overcoming such disadvantage, the applicant has proposed, in Japanese Patent application No. 89/228343, corresponding to European Patent application 90110605.4-2106, now published as EP-A-0400683, a powdered metal spray-coating material which comprises 40 to 60 % by weight of Ni, 20 to 40 % by weight of Co, 15 to 25 % by weight of Cr and 0,1 to 1,0 % by weight of Y, wherein a porous ceramic layer of  $ZrO_2/Y_2O_3$  is provided on the metal spray-coating material.

However, the porous ceramic layer spray-coated on the inner surface of a mold may be peeled off in long term runs of 30.000 shots or more of casting, and therefore, it has been desired to provide a further increased bonding force to the metal spray-coated layer.

Thereupon, the applicant has made zealous studies for a ceramic spray-coating material with a further increased bonding force and consequently has found that the above disadvantage can be avoided by increasing the purity of a ceramic spray-coating material of  $ZrO_2/Y_2O_3$ .

Summary of the invention

Therefore, the present invention provides a ceramic spray-coating material comprising zirconia and yttria, wherein the purity of a mixture of zirconia and yttria is 99,6% by weight or more.

The ceramic spray-coating material according to the present invention has an excellent bonding

force, as compared to the prior art material.

Detailed description of the invention

The composition of the ceramic spray-coating material according to the present invention comprises 98 to 85 % by weight of  $ZrO_2$  and 2 to 15 % by weight of  $Y_2O_3$ . The particles of the spray-coating material may be of an average particle size in a range of 20 to 40  $\mu$ m, but an average particle size in a range of 10 to 50  $\mu$ m is particularly desirable.

When used in a mold, a ceramic layer formed of such spray-coating material serves to eliminate a gas during casting and in addition thereto, to considerably improve the heat resistance and durability of the mold. In general, it is preferable that the thickness of such layer is in a range of 50 to 500  $\mu$ m.

The ceramic spray-coating material according to the present invention will now be described as being used, by way of an example, in a convenient production of a discontinuous casting mold of a copper alloy. An Ni-plating layer is formed on an inner surface of the copper alloy mold in an usual manner to a thickness of 50 to 300 μm, preferably 100 to 200 µm. If necessary, a powder alloy of Ni/Co/Cr/Y as described in Japanese Patent application No. 89/228343, corresponding to European Patent application 90110605.4-2106, now published as EP-A-0400683, may be applied onto the Ni-plating layer, with cooling with a water-cooling device provided within the mold, to a thickness of 50 to 600  $\mu$ m, preferably 200 to 300  $\mu$ m by plasma spray-coating at a temperature of about 10.000 to about 5.000 °C or by jet coating at a temperature of about 2.700 °C. Then, a ceramic coating layer of the above-described composition with a high purity (of 99,6 % by weight or more) is applied to a thickness of 50 to 500 µm, preferably 200 to 300  $\mu$ m by a spray coating under a similar condition. A large number of open pores are produced in the ceramic layer and render the ceramic layer porous. The pores providing the porosity are of a size small as they can be observed by a microscope, rather than a size as large as they will cause a ruggedness on a surface of a molded product.

The copper alloy mold made in this manner has the porous ceramic layer having open pores which serve to contain a gas generated during casting and to guide the gas outside and hence, any adverse affection due to the gas cannot be exerted to the surface of a molded product. In other words, no blow (ruggedness) is produced.

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When the ceramic layer is employed in a copper alloy mold, the mold has higher durability and wear resistance, which enables the number of runs of casting corresponding to the number of shots, approximately 30 to 50 % more than the number of runs of 30.000 shots when a lower purity ceramic layer is used, e.g., 40.000 shots or more, without need for applying a soft facing material to the inner surface of the mold.

The present invention will now be described in more detail by way of Example and Comparative Example.

## Example

An Ni-plating layer having a thickness of 200  $\mu$ m is provided, by electro-plating, on an inner surface of a mold made of a copper alloy containing 0,15 % by weight of zirconium and having a coefficient of thermal conductivity of 7. Then, an alloy comprising 57,55 % by weight of Ni, 25 % by weight of Co, 17 % by weight of Cr and 0,45 % by weight of Y is spray-coated at 8.000  $^{\circ}$  C by a plasma spray-coating process to form a coating film of 150  $\mu$ m.

A ceramic mixture having a purity of 99,71 % by weight and comprising 91,41 % by weight of  $ZrO_2$ , 8,3 % by weight of  $Y_2O_3$ , 0,08 % by weight of  $SiO_2$ , 0,03 % by weight of  $Fe_2O_3$  and 0,18 % by weight of impurities is applied onto the thus-formed Ni/Co/Cr/Y alloy coating film to a thickness of 250  $\mu$ m by a similar spray-coating process. The spray-coating temperature in this spray-coating is of 8.000 °C. A large number of very small pores are present in the ceramic layer, thereby providing a porosity.

When the permanent mold made in this manner was used in casting of a magnesium alloy casing for an automobile engine while being cooled to a temperature of 350 to 400 °C, and even if 40.000 shots were conducted, any change on the surface of the mold was still not observed and the surface profile of a molded product was good.

### Comparative Example

A permanent mold is made in the same manner as in Example 1, except for use of a ceramic mixture having a purity of 98,93 % and comprising 90,78 % by weight of  $ZrO_2$ , 8,15 % by weight of  $Y_2O_3$ , 0,38 % by weight of  $Al_2O_3$ , 0,20 % by weight of  $SiO_2$ , 0,11 % by weight of  $Fe_2O_3$  and 0,38 % by weight of impurities. The resulting permanent mold had its ceramic layer peeled off a 30.451 runs.

## Claims

 A ceramic spray coating material comprising zirconia and yttria, wherein the purity of a mixture of zirconia and yttria is 99,6% by weight or more.

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