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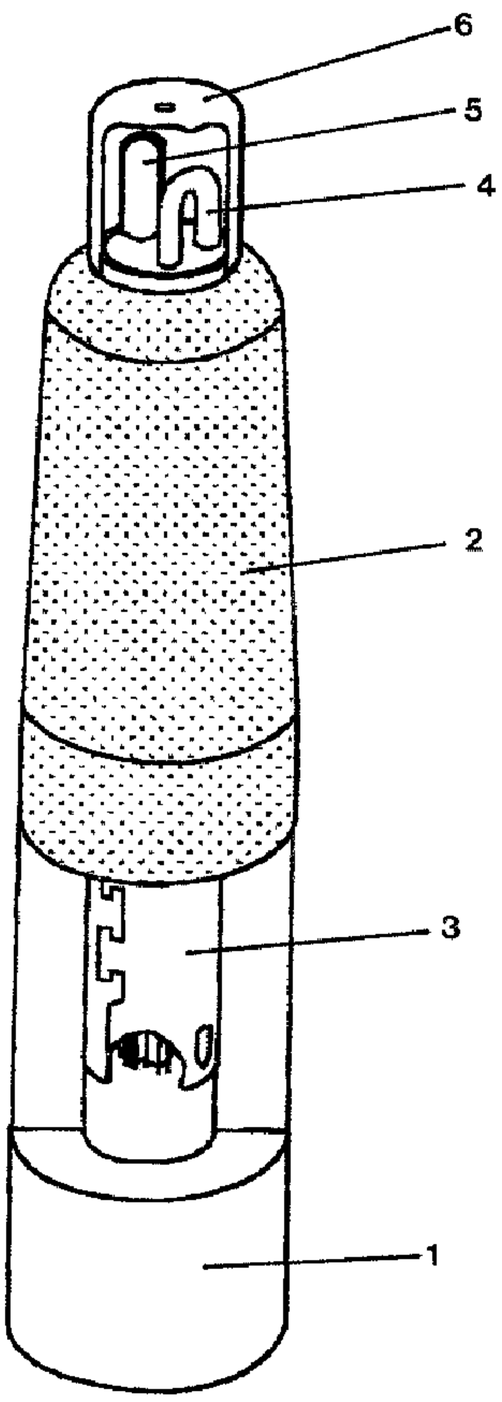
(54) Titre : DISPOSITIF DE MESURE POUR DETERMINER L'ACTIVITE DE L'OXYGENE DANS DU LAITIER OU DU METAL FONDU

(54) Title: MEASUREMENT DEVICE FOR DETERMINING OXYGEN ACTIVITY IN MOLTEN METAL OR SLAG



(57) Abrégé/Abstract:
The invention relates to a measurement device for determining the oxygen activity in molten metal or slag with a measurement head, which is arranged at one end of a carrier tube and on which an electrochemical measurement cell is arranged. The

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(57) Abrégé(suite)/Abstract(continued):
electrochemical measurement cell has a solid electrolyte tube, which is closed at one end and which contains a reference material and an electrode at its closed end. The electrode projects from the opposite end of the solid electrolyte tube. The invention also relates to a corresponding solid electrolyte tube. The invention is characterized in that the outer surface of the solid electrolyte tube has a coating of a mixture of calcium zirconate with a fluoride.

Abstract

The invention relates to a measurement device for determining the oxygen activity in molten metal or slag with a measurement head, which is arranged at one end of a carrier tube and on which an electrochemical measurement cell is arranged. The electrochemical measurement cell has a solid electrolyte tube, which is closed at one end and which contains a reference material and an electrode at its closed end. The electrode projects from the opposite end of the solid electrolyte tube. The invention also relates to a corresponding solid electrolyte tube. The invention is characterized in that the outer surface of the solid electrolyte tube has a coating of a mixture of calcium zirconate with a fluoride.

Patent Application

Measurement Device for Determining Oxygen Activity in Molten Metal or Slag

The invention relates to a measurement device for determining the oxygen activity in molten metal or slag with a measurement head, which is arranged at one end of a carrier tube and on which an electrochemical measurement cell is arranged. The electrochemical measurement cell has a solid electrolyte tube, which is closed on one end and which contains a reference material and an electrode at its closed end, wherein the electrode projects out of the opposite end of the solid electrolyte tube. In addition, the invention relates to a solid electrolyte tube for an electrochemical measurement cell.

Such measurement devices are known, for example, from DE 31 52 318 C2. The sensor described in this document is used to measure the concentration of oxygen in molten metal. Similar measurement devices are also known from US 3,578,578, DE 28 10 134 A1, or DE 26 00 103 C2.

In addition to oxygen, there is the need to measure other materials contained in molten metals. Therefore, the invention is based on the object of providing a simple measurement device and also a corresponding solid electrolyte tube, with which, in addition to the oxygen content, the concentration of other elements can also be determined.

The object is achieved in that the outer surface of the solid electrolyte tube has a coating of a mixture of calcium zirconate with a fluoride. It has been shown that this coating allows the determination of the concentration, for example, of sulfur, silicon, or carbon in melts. The effect can be explained in that the sulfur, for example, found in the liquid metal reacts with the CaO from the calcium zirconate, producing oxygen as a reaction product, and the change of the oxygen activity at the surface of the solid electrolyte is measured and correlated with the sulfur. The measurement device can be used in molten metal or slag, especially in steel or iron melts, for measuring the concentration of sulfur, silicon, or carbon. A quick measurement is obtained thereby. It is advantageous if the measurement device has, in addition to the electrochemical measurement cell, a temperature sensor, for example a thermocouple, so that the temperature of the molten metal can also be measured. Silicon is correlated with the sulfur content. Carbon can be calculated from the silicon-carbon thermal equilibrium of the molten metal.

With the measurement device according to the invention, a sample analysis in the laboratory can be avoided, so that considerable savings of time in the production process and consequently an improved and quicker influence of production process can be achieved.

Advantageous embodiments of the invention are given in the dependent claims. It is expedient that the fluoride be at least one from the group of CaF_2, NaF, SrF_2, BaF_2, MgF_2. It is advantageous for high measurement sensitivity that the calcium zirconate be stoichiometric. Likewise, it is advantageous that the coating have a thickness of approximately 10-100 μm, especially 30 μm. Here, a thinner layer is sufficient at higher temperatures of use (for example, before a desulfurization treatment). Here, the response time is rather short. At lower temperatures of use (for example, after the desulfurization treatment) a thicker coating is required. The response time is then somewhat longer.

The solid electrolyte tube is advantageously stabilized ZrO_2. The layer can also only partially cover the outer surface of the solid electrolyte tube, wherein at least the surface of the tube in the region, in which the reference mass is arranged, should be coated.

In the following, an embodiment of the invention is explained with reference to the drawing. Shown in the drawing are:

Figure 1, a measurement device and

Figure 2, the cross section through a solid electrolyte tube.

The measurement device has a carrier tube 1, in which the measurement head 2 is held, wherein the measurement head 2 connects inside the carrier tube 1 to a supply line to the measurement and evaluation devices through a contact piece 3. The carrier tube 1 is shown only at its beginning in Figure 1.

At the immersion end of the measurement head, in addition to a thermocouple 4, there is a solid electrolyte tube 5. Thermocouple 4 and solid electrolyte tube 5 are surrounded by a protective cap 6 and are each protected before and during the immersion of the measurement head into the melt, particularly molten iron or steel.

In Figure 2 the solid electrolyte tube 5 is shown in section. It is produced from stabilized zirconium dioxide and has in its interior a mixture of chromium and chromium dioxide as a reference material 7. The filling material 8 arranged on top of this mixture is aluminum oxide, for example. In the center of the solid electrolyte tube 5 there is arranged a molybdenum rod as electrode 9. The electrode 9 projects from the open end

of the solid electrolyte tube 5. This open end is closed by a cap 10, wherein the filling material 8 is held at its upper end by a gas-permeable cement 11. The solid electrolyte tube 5 is surrounded by a steel cap 12, which also protects the tube during the immersion in the molten metal. It then melts and exposes the coating 13 arranged on the solid electrolyte tube 5. The coating is preferably a mixture of calcium zirconate and magnesium fluoride.

In the melt CaO reacts with sulfur with formation of CaS, whereby oxygen is released, whose activity is measured with the aid of the solid electrolyte tube.

Claims

1. Measurement device for determining the oxygen activity in molten metal or slag with a measurement head, which is arranged at one end of a carrier tube and on which an electrochemical measurement cell is arranged, wherein the electrochemical measurement cell has a solid electrolyte tube, which is closed on one end and which contains a reference material and an electrode at its closed end, wherein the electrode projects from the opposite end of the solid electrolyte tube, characterized in that the outer surface of the solid electrolyte tube (5) has a coating (13) of a mixture of calcium zirconate with a fluoride.

2. Measurement device according to Claim 1, characterized in that the fluoride is at least one from the group of CaF_2, NaF, SrF_2, BaF_2, MgF_2.

3. Measurement device according to Claim 1 or 2, characterized in that the calcium zirconate is stoichiometric.

4. Measurement device according to one of Claims 1 to 3, characterized in that the coating (13) is 10 to 100 μm thick.

5. Measurement device according to one of Claims 1 to 4, characterized in that the coating (13) only partially covers the outer surface of the solid electrolyte tube (5).

6. Solid electrolyte tube for an electrochemical measurement cell with a closed end, characterized in that it has on its outer surface a coating (13) of a mixture of calcium zirconate with a fluoride.

7. Solid electrolyte tube according to Claim 6, characterized in that the fluoride is at least one from the group of CaF_2, NaF, SrF_2, BaF_2, MgF_2.

8. Solid electrolyte tube according to Claim 6 or 7, characterized in that the calcium zirconate is stoichiometric.

9. Solid electrolyte tube according to one of Claims 6 to 8, characterized in that the coating (13) is 10 to 100 μm thick.

10. Solid electrolyte tube according to one of Claims 6 to 9, characterized in that the coating (13) only partially covers the outer surface.

11. Use of the measurement device according to one of Claims 1 to 5 for determining the content of sulfur, silicon, or carbon in molten metal or slag, especially in steel or iron melts.

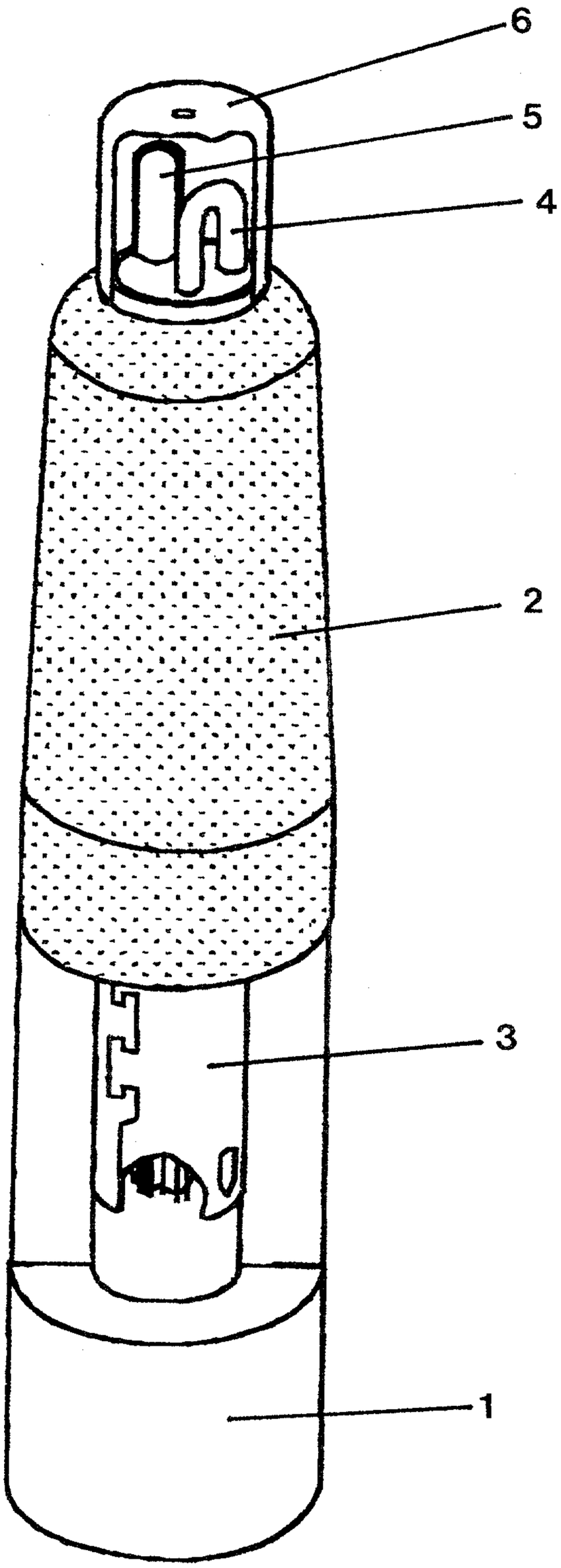


Fig. 1

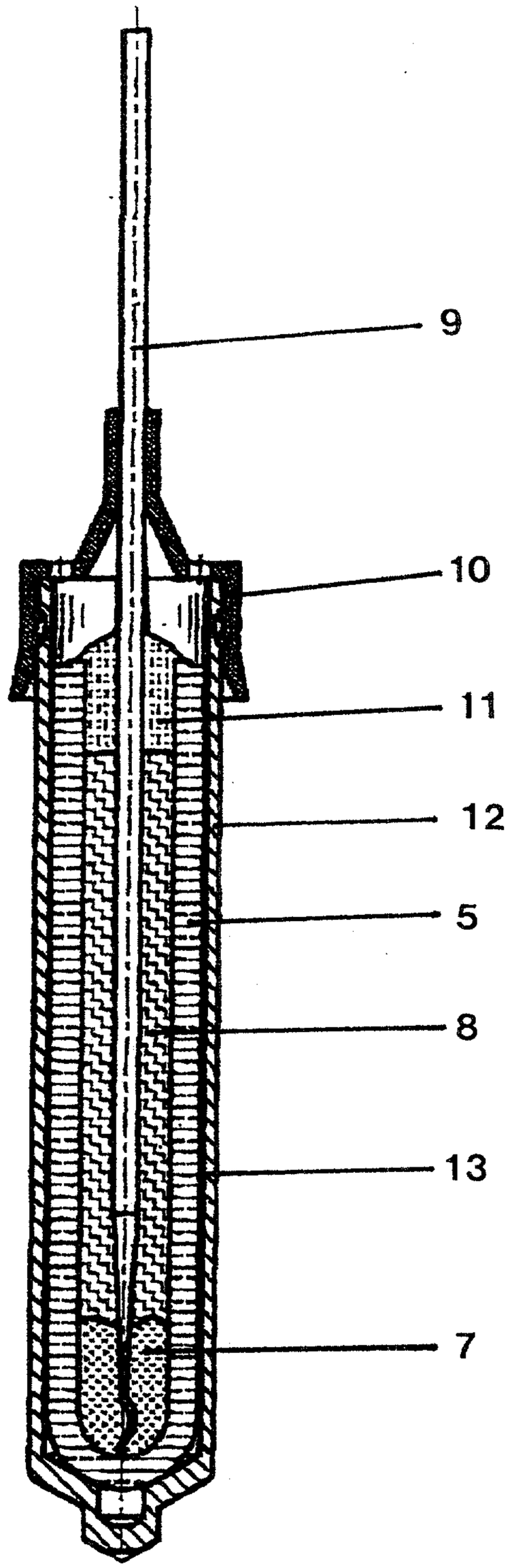
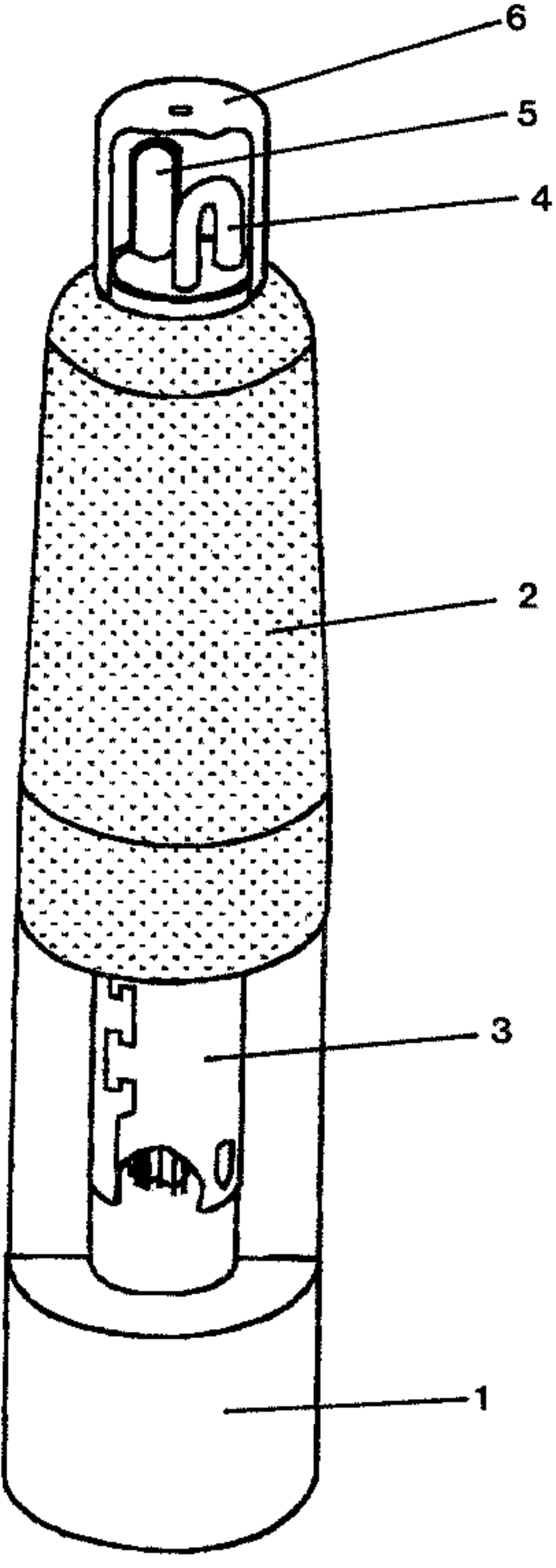


Fig. 2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