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(54) Title: DEVICE AND METHOD FOR CONTROLLING NON-IRON MELTING PROCESS

(57) Abstract: A furnace (10) for non-iron metals and a method of operating it are disclosed with a monitoring system (12) for monitoring in-situ the concentration of a passivation fluid,such as perfluoroketones in a cover gas(136). The monitoring system (12) includes a sensor (122) for determining an emission and/or an absorption of the passivation fluid at least one wavelength or wave- length band of the electromagnetic wave spectrum, with the measured concentration being used as a control input for a flow control system (13) controlling the supply of the cover gas (136) into the furnace (10).

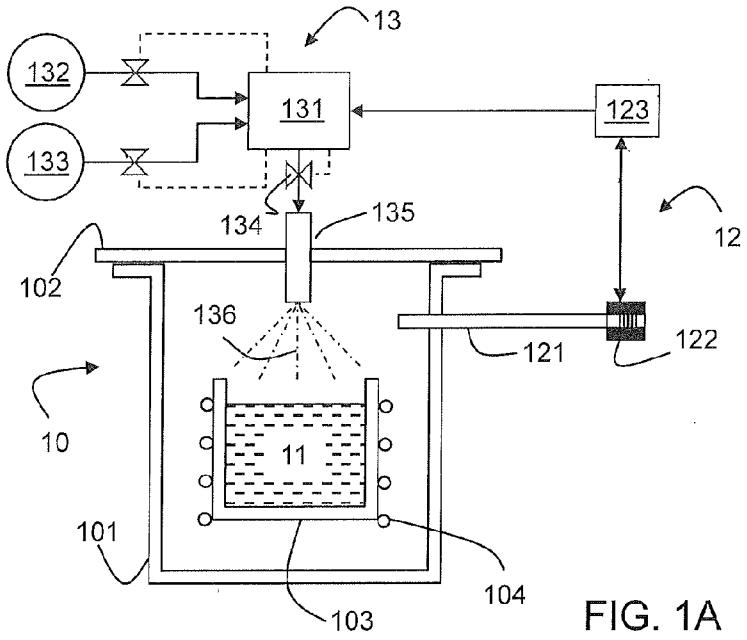


FIG. 1A

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Device and Method for Controlling Non-Iron Melting Process

FIELD OF THE INVENTION

The present invention relates to a device and a method for controlling melting processes for non-iron metals, particularly for controlling a gas passivation layer in a furnace for melting non-iron metals or alloys.

BACKGROUND OF THE INVENTION

The protection of liquid metals from oxidation is a major issue in recycling and melting processes in the light metal industry. For the protection of the liquid metal surface, gases which produce a thin passivation film at the liquid/gas interface are frequently used. The passivation layer avoids violent reaction of the metal with oxygen in the surrounding air. Passive gases like SF_6 or SO_2 are commonly employed for magnesium melts, however, they are being phased out, because they cannot meet environmental standards due to their extremely high global warming potentials (GWP), toxicities or corrosion potentials. As alternative cover gases, in particular for magnesium melting, gases like HFC-134a (CF_3CFH_2), Novec 612 (a perfluoroketone or PFK) and BF_3 mixed with a carrier gas (such as for example air or CO_2) have been successfully tested as described for example in: “Magnesium melt protection by covering gas”, M. Holtzer, A. Bobrowski, ARCHIVES of FOUNDRY ENGINEERING Volume 8, Special Issue 1/2008, p. 131-1 36. For example the company 3M produces the fluoroketone Novec™ 612 (abbreviated herein as C6) and merchandises it as Magnesium Protection Fluid.

During the recycling, melting or casting processes it is very important to keep the cover gas concentration at an optimum level, i.e. to provide enough to fulfill the requirements as cover gas (at conservative cover gas usage levels), but as little as possible to

protect the environment. When a furnace hatch is opened to add ingots, to remove dross or to take samples, the gas of the head space escapes quickly and the cover gas is diluted with incoming environmental air. If the concentration of cover gas in the head space is too low, the protecting film is not homogeneously closed and violent reactions with oxygen can occur. If the concentration is too high, too much dross is produced and the process is not economical anymore. Thus, from economical, safety and environmental aspects the concentration of cover gas in the head space above the molten metal must be monitored and readjusted to ensure optimum process conditions.

It is known to analyze the cover gas with complex extractive systems, such as Fourier-Transform infrared spectrometry (FTIR) or a residual gas quadrupole mass analyzer. Cover gas emission measurements of this kind were for example reported from US Environmental Protection Agency for magnesium alloy ingot casting environments, to study the greenhouse gas emissions and occupational exposure in: "Characterization of Cover Gas and Byproduct Emissions from Secondary Magnesium Ingot Casting", EPA report, EPA 430-R-08-008. These methods are too expensive and fragile for industrial monitoring, and particularly for continuous on-line monitoring.

A method to indirectly measure the required amount of cover gas for sufficient protection is outlined in the European patent application EP 1 918 044 A1. Therein a concept is used that is based on the sensing of either moisture or oxygen content in the cover gas head space. This output is used subsequently for indirectly deducing the PFK concentration.

Another indirect measurement is applied in magnesium melt protection methods using CO_2 snow. For the monitoring of the oxygen content in the cover gas phase an oxygen analyzer is used as described for example in: "Magnesium alloy melt protection by high-efficiency phase

transition of carbon dioxide", S.-C.Yang and Y.-C. Lin, Journal of Cleaner Production 41 (2013) p.74-78.

In the product brochure "3M™ Novec™ 612 Magnesium Protection Fluid" issued 07/2010, the concentration of cover gas including C6 is reestablished by increasing the flow rate of the cover gas when opening the hatch of the furnace. An automated approach for increasing the flow rate of the cover gas is suggested when adding ingots.

SUMMARY OF THE INVENTION

In view of the prior art it is an objective of the invention to provide an improved device and method for monitoring the concentration of passivation fluids within a carrier gas for use as cover gas in non-iron furnaces and further to provide an improved and a more accurate control and dosage system for cover gas in a non-iron furnace. This objective is achieved by the subject-matter of the independent claims. Embodiments arise from dependent claims, their combinations, and from the description and the figures.

Hence, according to a first aspect of the invention, there is provided a furnace for melting non-iron metals or alloys thereof, particularly magnesium and/or aluminum and their alloys, with a monitoring system for monitoring in-situ the concentration of a passivation fluid within a cover gas, with the monitoring system including a sensor for determining a concentration-dependent electromagnetic property of the passivation fluid molecules at at least one wavelength or wavelength band of the electromagnetic wave spectrum.

In an embodiments, the determining the concentration-dependent electromagnetic property comprises determining an emission and/or an absorption and/or a transmission and/or a scattering by the passivation fluid molecules.

The system thus monitors the concentration directly, i.e. based on the measurement of a response of the molecules of the passivation fluid to electromagnetic radiation, preferably in form of an attenuation or a transmission measurement.

In embodiments, the monitoring system is mounted stationary and monitors the concentration continuously, quasi-continuously, or at least at intervals of less than 1 hour, in particular at intervals of less than 10 minute or even less than 1 minute.

In embodiments, the passivation fluid is an organic fluorine compound, in particular a partly fluorinated or fully fluorinated (=perfluorinated) compound of an olefine, alkane, ketone or polyketone, ether or polyether, and any mixtures thereof. Most preferred embodiments are perfluoroketones having from 5 carbon atoms to 9 carbon atoms that shall be monitored. Examples of the perfluoroketones having from 5 carbon atoms to 9 carbon atoms include $CF_3CF_2C(O)CF(CF_3)_2$, $(CF_3)_2CFC(O)CF(CF_3)_2$, $CF_3(CF_2)_2C(O)CF(CF_3)_2$, $CF_3(CF_2)_3C(O)CF(CF_3)_2$, $CF_3(CF_2)_5C(O)CF_3$, $CF_3CF_2C(O)CF_2CF_2CF_3$, $CF_3C(O)CF(CF_3)_2$, and perfluorocyclohexanone and others as referred to in this specification. These compounds may be used alone or in combination with one another, and/or in mixtures with a carrier or background gas.

In an embodiment of this aspect of the invention, the at least one wavelength or wavelength band is in the range of 200 nm to 20000 nm, more preferably in the range of 200 nm to 400 nm and/or 1850 nm to 1950 nm and/or 5000 nm to 20000 nm.

In embodiments, the sensor includes a radiation source and/or a spectral filter that is or are tuned each or both in combination to at least one wavelength or wavelength band in the spectral range of 200 nm to 20000 nm, for example in at least one of the spectral ranges of 200 nm to 400 nm, 1850 nm to 1950 nm and 5000 nm to 20000 nm.

In embodiments, the passivation fluid comprises at least one component selected from the group consisting of:

partially or fully fluorinated ethers; in particular: hydrofluoroethers, hydrofluoro monoethers, hydrofluoro monoethers containing at least 3 carbon atoms, perfluoro monoethers, perfluoro monoethers containing at least 4 carbon atoms, fluorooxiranes, perfluorooxiranes, hydrofluorooxiranes, perfluorooxiranes comprising from three to fifteen carbon atoms, hydrofluorooxiranes comprising from three to fifteen carbon atoms, and mixtures thereof;

- partially or fully fluorinated ketones; in particular: hydrofluoro monoketones, perfluoro monoketones, perfluoro monoketones comprising at least 5 carbon atoms, and mixtures thereof;

fluoroolefins; in particular: perfluoroolefines, hydrofluoroolefins (HFO), hydrofluoroolefins (HFO) comprising at least three carbon atoms, hydrofluoroolefins (HFO) comprising exactly three carbon atoms, trans-1,3,3,3-tetrafluoro-1-propene (HFO-1234ze), 2,3,3,3-tetrafluoro-1-propene (HFO-1234yf), and mixtures thereof; and

- mixtures thereof.

In embodiments, the sensor includes a part extending into the furnace or a window for transmitting radiation into and/or receiving radiation out of the furnace. Alternatively, the sensor can include a part extending into a by-pass or extraction pipe being in a fluid connection with the furnace or its head space, and/or the sensor can include a window for transmitting into and/or receiving radiation out of the by-pass or extraction pipe. In further embodiments, the by-pass or extraction pipe can be temperature-controlled. The by-pass or extraction pipe can further include a pressure reducer for reducing the pressure at a point where the sensor has an interface to the by-pass or pipe.

In embodiments, the monitoring system, in particular the sensor, comprises an insulation-fluid-permeable and particle-impermeable protective cover, that separates the monitoring device, in particular an optical beam and/or optical components of the sensor, from a surrounding region inside the furnace or outside the furnace.

In other embodiments, the monitoring system, in particular the sensor, comprises an optical measurement channel or beam at a first wavelength (e.g. that is absorbed by the first fluid component (A)), and an optical reference channel or beam at a second wavelength that is not modified, in particular not absorbed, by the passivation fluid, in particular fluoroketone.

In a further embodiment of this aspect of the invention, the monitoring system is part of or is connected to a flow control system delivering a cover gas to the furnace and being connected to a supply of the passivation fluid, in particular to a supply of passivation fluid mixed with a carrier gas, or being connected to separate supplies of both passivation fluid and a carrier gas. In an embodiment of this variant, the flow control system includes one or more nozzles for injecting the passivation fluid or the passivation fluid mixed with a carrier gas into the furnace and in particular into its head space.

The concentration of the passivation fluid in the cover gas mixture, i.e. when mixed with the carrier gas, is typically in a range of 100 ppm to 2000 ppm.

In embodiments, the device is best combined with one or more further sensors monitoring for example an oxygen content, and/or a moisture level, and/or carrier gas concentration.

According to a second aspect of the invention, there is provided a method for controlling a furnace for melting non-iron metals and alloys, particularly magnesium or aluminum and their alloys, the method in-

cluding the step of monitoring in-situ a concentration of a passivation fluid in a cover gas by determining a concentration-dependent electromagnetic property of passivation fluid molecules at at least one wavelength or wavelength band of the electromagnetic wave spectrum.

In an embodiment, the determining the concentration-dependent electromagnetic property comprises determining an emission and/or an absorption and/or a transmission and/or a scattering by the passivation fluid molecules.

In an embodiment of this aspect of the invention, the method includes a further step of delivering a cover gas to the furnace by controlling a supply of the passivation fluid, in particular a supply of the passivation fluid mixed with a carrier gas or separate supplies of both the passivation fluid and a carrier gas. In an embodiment of this variant, one or more nozzles for injecting the passivation fluid or the passivation fluid mixed with a carrier gas into the furnace or the head space of the furnace are operated as a function of the in-situ measurements of the concentration of the passivation fluid molecules, in particular as a function of a determined emission light power and/or absorption light power of the passivation fluid molecules at the at least one wavelength or wavelength band of the electromagnetic wave spectrum.

In an embodiment, the method comprises the method elements of: measuring the concentration of the passivation fluid at a first wavelength, and correcting the measurement by using a second wavelength that is not absorbed by the passivation fluid, in particular fluoroketone.

The above and other aspects of the present invention together with further embodiments and applications of the invention are described in further details in the following description and figures.

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1A, 1B, 1C are schematic diagrams of exemplary devices for controlling the cover gas in a furnace in accordance with three embodiments of the invention; and

FIG. 2 is a flow chart with method steps in accordance with an exemplary embodiments of the invention; and

Fig. 3 shows an optical sensor with an optical measurement channel and an optical reference channel.

DETAILED DESCRIPTION

FIG. 1A shows a schematic diagram of a device for controlling the cover gas 136. Apart from the actual furnace part 10 the device includes a sensor part 12 and a flow control part 13.

The furnace 10 has the typical components of a melting furnace 10 for preparing a melt 11 of a non-iron metal or a non-iron metal alloy based for example on magnesium or on aluminum as main component. The furnace wall 101 and the lid 102 house a crucible 103 which is heated using a heater 104. It can for example be part of an automated industrial robotic system supporting the process of die casting, lost foam, core handling and cleaning (not shown).

The sensor part 12 can for example be located at least with one part or an extension close to the head space of the furnace 10. In the example shown it includes a temperature-controlled gas extraction tube 121. The tube 121 forms a connection allowing a flow of fluid between the head space of the furnace 10 and the position of an optical sensor 122. Connected to the tube 121 is a pump (not shown) to drive a gas flow from the head space to the position of the sensor 122.

The sensor 122 can for example be a radiation source paired with a photo detector positioned across a

measuring chamber or both positioned on one side of the measuring chamber with the juxtaposed side of the measuring chamber being covered with a mirror to reflect radiation from the source and hence doubling the optical path of the radiation through the sample of cover gas 136 in the measuring chamber. The wavelength or wavelength band at which the sensor operates can be in the UV, in the near-IR or the mid-IR range or more specifically in at least one of the spectral ranges of 200 nm to 400 nm, 1850 nm to 1950 nm, and 5000 nm to 20000 nm, or any combination of those.

The UV band can be accessed using as light source 12 a gas discharge lamp, e.g. a deuterium lamp as commercially available (e.g. Ocean Optics DT-Mini-2-GS with appropriate filter), or UV LEDs that emit in a narrow spectral region, as commercially available for example from Mightex, Toronto, Ontario Canada. Other UV light sources which can be used are excimer lamps (Xe) and NOx lamps (e.g. commercially available from Heraeus Noblelight or Analytical Control Instruments GmbH Berlin, Germany). The detector 13 for the UV band can be based on SiC photodiodes, as commercially available for example from Roithner Lasertechnik GmbH, Vienna, Austria.

The NIR band can be accessed using as light source 12 incandescent or quartz halogen light bulbs, NIR LEDs or VCSELs (vertical cavity surface emitting laser), all of which are commercially available. The detector 13 for the NIR band can be based on Si or InGaS photodetectors that are also commercially available.

For generating radiation in the mid-IR range the source 12 can include a broad-band, incandescent light source (e.g. a radiating filament) with a notch filter permitting the transmission of only selected wavelengths that interrogate a narrow spectral region in which the respective molecules of the passivation fluid, such as for example a perfluoroketone, absorb. Other sources can include QCL (quantum cascade lasers) or lead salt diode la-

sers, as are known per se and are commercially available. The detector 13 for the MIR band can be based on PbS photodetectors, that are also commercially available.

An emission can be monitored for example by exciting the molecules of the passivation fluid, e.g. a perfluoroketone such as C5 (fluoroketone, in particular fluoromonoketone and/or perfluoroketone, comprising exactly 5 carbon atoms) or C6, at a wavelength around 300 nm and observing fluorescence in a band from 390 nm to 490 nm, particularly at around 420 nm.

The sensor 12 is controlled by a sensor control system 123. The control system 123 is used to read out the sensor 122 and to convert the result of the optical measurement into values for the flow control part 13. The control system 123 can also be used for the general operation of the sensor 122, its calibration and other adjustments to it.

The flow control part 13 includes a flow controller 131 receiving input signals from the sensor controller 123. The flow controller 131 controls the supply of the cover gas 136, which in the example shown is drawn from a reservoir 132 for the passivation fluid, e.g. a perfluoroketone such as C5, C6, or C7 (fluoroketone, in particular fluoromonoketone and/or perfluoroketone, comprising exactly 7 carbon atoms) and a reservoir 133 for the carrier gas, e.g. CO_2 or pressurized air. The flow controller 131 further includes a mixing chamber (not shown) connected to the two reservoirs 132, 133 and to one or more nozzles 135 used to spray the cover gas 136 over the surface of the melt 11 in the crucible 103.

The flow controller 131 can control the control valve 134 for the nozzle 135 and hence determine the amount of cover gas 136 to be sprayed onto the surface of the melt 11. By using additional valves (not shown) between the mixing chamber (not shown) and the two reservoirs 132, 133, the flow controller 131 can further be used to change the concentration of the passivation fluid in the cover gas 136.

To control the dosage of the cover gas 136 above the melt 11, the above device 12, 13 can be operated as a feedback control circuit, e.g. as a proportional-integral-derivative controller (PID controller) or the like. As illustrated in FIG. 2, a desired concentration level of a perfluoroketone in the head space above the melt 11 or any equivalent of it can be set as reference value (step 21). The flow controller 131 calculates an "error" value as the difference between a directly or in-situ measured concentration of perfluoroketones (step 22) and the desired reference value or setpoint (step 23) and attempts to minimize the error by adjusting the flow through the nozzle 135 (step 24).

Regarding the UV range of wavelengths it is known that C6 has a peak absorption at around 300 nm. It has further been found that the absorption peak for C5 in this range is shifted by about 5 nm, and the absorption peak value for C7 is even closer to the one of C6. The strong absorption cross-section and the specificity to ketones make this band a preferred candidate for optical monitoring across a range of possible cover gases 136. On the contrary the visible region does not seem suitable for optical absorption measurements at least for these perfluokoketones C5, C6 and C7, as no absorption feature in the wavelength regime between 400 nm and 1100 nm was identified.

With regard to the near-infrared (NIR) spectral range it is found that C6 shows an absorption peak at 1891 nm, while C5 and C7 show two overlapping absorption peaks at 1873 nm / 1882 nm and 1894 nm / 1903 nm, respectively. There is no cross interference of the C5 absorption bands with those of CO_2 in the NIR region; and O_2 does not have a permanent dipole moment and therefore does not exhibit a vibration spectrum in the infrared at all. The spectra of CO_2 (HITRAN data base) show a significant band at 1960 nm and at 2000 nm, which however do not overlap with the above-mentioned fluoroketone bands.

Water absorption lines can interfere with the C5 absorption line, but this depends on the specific optical setup of the analyzer (e.g. the spectral width of detection). Whether water interference causes a problem for the C5 detection of course depends on the relative absorption strength of the lines and the relative concentrations of C5 and water. However, according to this invention, water interference can be avoided completely by choosing appropriate sharp, narrow absorption features of for example C5 (or C6 or C7) that show no spectral overlap with the absorption features of water.

With regard to the mid-infrared (MIR) spectral range it is found that in the spectral region between 2000 cm-1 (5 μm) and 500 cm-1 (20 μm) C5 shows absorption bands between 600 cm-1 and 1900 cm-1. They presumably stem from vibrational transitions of the carbon framework (below about 1100 cm-1), of the C-F bonds (1100 cm-1 to 1400 cm-1) and the C=O carbonyl group (1800 cm-1). In the spectral region from 2000 cm-1 to 4000 cm-1, C5 does not display any absorption features. Some of the above-mentioned bands can be used for quantification of C5 by IR absorption.

It is advantageous to reduce cross-sensitivity to other species that may be present, such as water vapor, a carrier gas CO_2 and the expected decomposition products HF, CF_4, hexafluoropropene, heptafluoropropane. With respect to these species, particularly suitable bands for the detection of C5 is or are those at around 990 cm-1 and/or at around 873.5 cm-1; and/or a suitable band for the detection of C6 is at around 1024 cm-1.

Generally, a suitable wavelength or wavelength band for measuring the concentration of the passivation fluid directly or in-situ can be established by comparing the respective spectra of the passivation fluid molecules, of the carrier gas molecules and of any gaseous reaction products of such molecules in the head space of the furnace 10.

A further example of the present invention is illustrated in FIG. 1B. The elements of the device identical or similar to those of FIG. 1A are denoted using the same reference numerals. In the example the sensor part 12 includes a radiation source 122-1 and a photo receiver 122-2 which are separated such that the optical path crosses the head space above the melt 11 through the cover gas 136. The radiation passes through windows or filters 121-1, 121-2 within the wall 102 of the furnace 10.

A further example of the present invention is illustrated in FIG. 1C. The elements of the device identical or similar to those of FIG. 1A are denoted using the same reference numerals. In the example the sensor part 12 includes a by-pass 124 through which a part of the cover gas 136 in the head space above the melt 11 is circulated. The by-pass 124 includes an optical sensor 122 as described above.

When a sample of the head space gas is extracted, such as through an extraction tube 121 or a by-pass 124, it can be important to maintain a constant temperature at the location where the measurement is performed. For that purpose the extraction tube 121 or a by-pass 124 can for example be provided with a heater and/or a cooler. This or these heater and/or cooler can be devices known in the art, e.g. resistance heaters, peltier elements, coolant pipes, etc..

Furthermore, it can be important at certain bands, such as the near infrared (NIR), to reduce the pressure of cover gas samples 136 from atmospheric pressure to a much lower pressure, e.g. by a factor of 100 or more. Such a pressure reduction can be achieved using for example a throttle or pressure reducing valve (not shown) in the extraction tube 121 or the by-pass 124.

Due to the risk of formation of highly toxic perfluoroisobutene (PFIB), typically a small amount of oxygen is added to the CO_2 carrier gas stream to provide

a sink for perfluoroalkyl-radicals. This oxygen content can also be monitored optically using the near infrared line of molecular O_2 around 760 nm. This line can be accessed for example by commercially available VCSELs (vertical cavity surface emitting lasers). In this way, both the ketone and the oxygen content can be tracked by one measurement system using two light sources.

In further embodiments, the monitoring system, in particular the sensor, comprises an insulation-fluid-permeable and particle-impermeable protective cover (not specifically shown, but e.g. present in the optical path between 122-1 to 122-2 in Fig. 1B), that separates the monitoring device 12, in particular an optical beam and/or optical components of the sensor 122, from a surrounding region of the furnace 10, might it be inside the furnace 10 or outside the furnace 10. In particular, the protective cover is selected from at least one of the group consisting of:

* a sintered material,
* a porous material, in particular a porous metal,
* a gauze,
* a mesh,
* a membrane, in particular comprising a polymer material, and
* combinations thereof. Thus, an insulation-fluid-permeable and yet particle-impermeable protective cover is realized and the optical measurement is improved.

In embodiments, the protective cover (not explicitly shown) can be in the form of a protective cover plate, e.g. a plate separating the electromagnetic or optical sensor 122 or at least some of its optical elements and/or beam paths, in particular beam paths of a measurement channel and/or reference channel; or it can be in the form of a protective cover tube, e.g. a tube enclosing the optical sensor 122 or at least some of its optical elements and/or beam paths, in particular beam paths of a measurement channel and/or reference channel. Any

other form suitable to separate the optical sensor 122 fully or partly from particles in the furnace 10 is possible, as well.

Alternatively or in addition to the semipermeable protective cover, the optical sensor 122 can be cleaned or purged, e.g. intermittently, by using for example one of: a flow of nitrogen, fluid jets, wipers, vibrating piezo-crystals, etc..

Fig. 3 shows an embodiment of a monitoring system 12, in particular electromagnetic or optical sensor 122, with an optical measurement channel or beam at a first wavelength (e.g. that is modified, in particular absorbed, by the passivation fluid), and an optical reference channel or beam at a second wavelength that is not modified, in particular not absorbed, by the passivation fluid, in particular fluoroketone. Several factors could adversely affect the measurements:

- light source emission drift (wavelength and intensity e.g. due to aging, internal temperature and surrounding temperature)
- optical fiber transmission changes (e.g. due to bending losses, physical movement of fibers, stress, temperature)
- transmission changes at optical connectors (e.g. due to physical movement, mechanical shock, vibration, stress, temperature)
- transmission changes at optical interfaces (e.g. due to contamination)
- optical detector instability (e.g. due to aging)
- analyzer electronics instabilities (e.g. affected by electromagnetic interference or e.g. due to ageing).

The first five factors can be mitigated by using an optical reference channel integrated into the optical sensor 122.

A blue light source BS emitting at around 293 nm (open rectangles), i.e. within the absorption band of e.g. C5 as passivation fluid, is coupled to an optical fiber (not shown) which delivers the light to an optical probe (sensor head). Alternatively, the blue light source BS is directly mounted to an optical feedthrough directing the light through the measurement path (e.g. 122-1, 122-2) in fluid communication with the furnace 10 (see above).

Prior to being coupled into the optical fiber or the measurement path, part of the light from the blue light source BS is split off using an optical beam splitter BSP1 and is send to a blue reference detector BRD which measures the stability of the emitted light intensity of the blue light source BS.

To eliminate artifacts in the transmitted signal (such as changes in the fiber bending losses or the presence of particle contamination on the optical interfaces within the furnace 10), a reference channel is used.

Light at a slightly red-shifted wavelength (black beams) which is not absorbed by e.g. C5 as passivation fluid, i.e. at wavelengths $\lambda > 360$ nm, emitted by a red light source RS is used to interrogate the optical path for optical transmission changes. The emission stability of RS is recorded by a red reference detector RRD using a second beam splitter BSP2.

The red and blue light is combined (e.g. by a first dichroic mirror DM1). The red light traverses the same optical path (hatched beams) as the blue light, but is not absorbed by the passivation fluid (e.g. C5). When the red light returns from the sensor head, it is split off using a second dichroic mirror DM2 to the red light detector RD. To ensure that none of the red light falls onto the blue light detector BD and vice versa, a short pass filter FSP is arranged in front of the blue light detector BD and a long pass filter FLP is arranged in front of the red light detector RD.

The number density of the passivation fluid (e.g. C5) can be obtained from the transmitted intensities, and at the same time losses introduced in the optical paths and variations in the intensity of the light sources can be corrected for. In particular the following formula can be used:

$$I_{\mathrm{tr}}^{(b)} = t_{\mathrm{SP}} t_{\mathrm{DM}}^{(b)} \left\{ \left[\frac{t_{\mathrm{DM}}^{(b)} t_{\mathrm{BS}}^{(b)} I_{\mathrm{ref}}^{(b)}}{1 - t_{\mathrm{BS}}^{(b)}} + \frac{k}{2} \left(\frac{I_{\mathrm{tr}}^{(r)}}{t_{\mathrm{LP}} r_{\mathrm{DM}}^{(r)}} - \frac{r_{\mathrm{DM}}^{(r)} t_{\mathrm{BS}}^{(r)} I_{\mathrm{ref}}^{(r)}}{1 - t_{\mathrm{BS}}^{(r)}} \right) \right] e^{-\sigma l N} + \frac{k}{2} \left(\frac{I_{\mathrm{tr}}^{(r)}}{t_{\mathrm{LP}} r_{\mathrm{DM}}^{(r)}} - \frac{r_{\mathrm{DM}}^{(r)} t_{\mathrm{BS}}^{(r)} I_{\mathrm{ref}}^{(r)}}{1 - t_{\mathrm{BS}}^{(r)}} \right) \right\}$$

with

$I_{tr}^{(b)}$ = transmitted blue light intensity (falling onto blue light detector BD)

t_{SP} = transmissivity of short pass filter FSP

$t_{DM}^{(b)}$ = transmissivity of dichroic mirror DM1, DM2 for blue light

$t_{BS}^{(b)}$ = transmissivity of beam splitter BSP1 for reference blue light (to blue reference detector BRD)

$I_{ref}^{(b)}$ = reference blue light intensity (falling onto blue reference detector BRD)

k = conversion factor for wavelength dependence of optical losses, defined by $k = \Delta I_{loss}^{(b)} / \Delta I_{loss}^{(r)}$ with

$\Delta I_{loss}^{(b)}$ = blue light intensity losses on forward optical path to the gas (i.e. reduction of blue light intensity after BSP1 and DM1 by losses up to gas) and on the backward optical path from the gas to the detector BD (i.e. reduction of sensor return blue light intensity by losses) and

$\Delta I_{loss}^{(r)}$ = red light intensity losses on forward optical path to the gas (i.e. reduction of red light intensity after BSP1 and DM1 by losses up to gas) and on backward optical path from the gas to the detector RD (i.e. reduction of sensor return red light intensity by losses)

$I_{tr}^{(r)}$ = transmitted red light intensity (falling onto red light detector RD)

t_{LP} = transmissivity of long pass filter FLP

$r_{DM}^{(r)}$ = reflectivity of dichroic mirror DM1, DM2 for red light

$t_{BS}^{(r)}$ = transmissivity of beam splitter BSP2 for reference red light (to red reference detector RRD)

$I_{ref}^{(r)}$ = reference red light intensity (falling onto red reference detector RRD)

σ = absorption cross section of dielectric insulation fluid component A (e.g. C5)

l = absorption path length (in gas; in absorbing gas at at least one wavelength)

N = number density of dielectric insulation fluid component A (e.g. C5).

A periodic measurement, e.g. a pulsed measurement, is preferable to minimize temperature-induced drift effects on the light sources. In this context, it is practical to alternate between the red and the blue channel. Then, by time-gated detection (e.g. via a lock-in amplifier), the red light detector RD, one dichroic mirror and the filters FLP and FSP can be omitted using just one common detector for both beams, given that detector sensitivity at the different wavelengths is sufficient or similar and the ratio of those sensitivities is known.

Electronics, i.e. light source 122-1 and detector 122-2, can be arranged at the optical components. In this case, proper shielding from the furnace 10 is necessary, for example from heat and/or electromagnetic interference present in the furnace 10 or in the neighbourhood of the furnace 10. If electronics cannot be shielded from the furnace 10, a fiber optic link can be used. In that case the reference channel setup is particularly useful, if the fibers cannot be held rigidly in place. Alternatively or in addition, the fibers can be immobilized in a duct. In any case, whether the system requires fiber optic links depends on whether heat and/or electromagnetic interference is critical or not or can be shielded or not.

While there are shown and described presently preferred embodiments of the invention, it is to be understood that the invention is not limited thereto but may be otherwise variously embodied and practised within the scope of the following claims. In particular, disclosed device features herewith also disclose the corresponding method features, and disclosed method features herewith also disclose the corresponding device features.

LIST OF REFERENCE SIGNS

10	furnace, furnace part
101	furnace wall
102	furnace lid
103	crucible
104	heater
11	melt
12	monitoring system, sensor part
121	gas extraction tube
121-1, 121-2	radiation window, radiation filter
122	sensor, electromagnetic sensor, optical sensor
122-1	radiation source
122-2	photo receiver
123	optical sensor control
124	gas bypass
13	flow control part
131	flow controller
132	passivation fluid reservoir
133	carrier gas reservoir
134	control valve
135	nozzle
136	cover gas
21	setting reference value
22	measuring PFK concentration
23	deriving control value
24	injecting cover gas

Claims

1. A furnace (10) for melting non-iron metals or non-iron alloys, particularly magnesium or aluminium and their alloys, with a monitoring system (12) for monitoring in-situ the concentration of a passivation fluid in a cover gas (136), with the monitoring system (12) including a sensor (122) for determining a concentration-dependent electromagnetic property of passivation fluid molecules at at least one wavelength or wavelength band of the electromagnetic wave spectrum.

2. The furnace of claim 1, wherein the determining the concentration-dependent electromagnetic property comprises determining an emission and/or an absorption and/or a transmission and/or a scattering by the passivation fluid molecules.

3. The furnace of any one of the preceding claims, wherein the monitoring system (12) monitors the concentration of the passivation fluid continuously or at least at intervals of less than one hour, particularly less than 10 min and more particularly less than 1 min.

4. The furnace of any one of the preceding claims, wherein the at least one wavelength or wavelength band is in a range of 200 nm to 20000 nm.

5. The furnace of any one of the preceding claims, wherein the at least one wavelength or wavelength band is in at least one of the ranges: 200 nm to 400 nm, 1850 nm to 1950 nm and 5000 nm to 20000 nm.

6. The furnace (10) of any one of the preceding claims, wherein the sensor (12) comprises an extraction pipe (121), in particular a temperature-controlled extraction pipe (121), extending into the furnace (10).

7. The furnace (10) of any one of the preceding claims, wherein the sensor (12) comprises at least one window (121-1, 121-2) for transmitting radiation into the furnace (10) and/or for receiving radiation exiting from the furnace (10).

8. The furnace (10) of any one of the preceding claims, wherein the sensor (12) comprises a by-pass (124), in particular a temperature-controlled by-pass (124), in a fluid connection with the furnace (10), in particular in a fluid connection with a head space of the furnace (10), to circulate a part of the cover gas (136).

9. The furnace (10) of any one of the preceding claims, wherein the monitoring system (12) for monitoring in-situ the concentration of the passivation fluid in the cover gas (136) is part of or is connected to a flow control system (13) delivering the cover gas (136) to the furnace (10) and being in turn connected to a supply (132) of the passivation fluid.

10. The furnace (10) of claim 9, wherein the flow control system (13) controls one or more nozzles (135) for injecting the passivation fluid or the passivation fluid mixed with a carrier gas into the furnace (10), in particular into a head space of the furnace (10).

11. The furnace (10) of any one of the preceding claims, wherein the control system (12) includes at least one further sensor to monitor the concentration of carrier gas components and/or of oxygen.

12. The furnace (10) of any one of the preceding claims, wherein the passivation fluid is an organic fluorine compound, particularly a perfluoroketone.

13. The furnace (10) of any one of the preceding claims, wherein the passivation fluid is selected from the group consisting of:

partially or fully fluorinated ethers; in particular: hydrofluoroethers, hydrofluoro monoethers, hydrofluoro monoethers containing at least 3 carbon atoms, perfluoro monoethers, perfluoro monoethers containing at least 4 carbon atoms, fluorooxiranes, perfluorooxiranes, hydrofluorooxiranes, perfluorooxiranes comprising from three to fifteen carbon atoms, hydrofluorooxiranes comprising from three to fifteen carbon atoms, and mixtures thereof;

- partially or fully fluorinated ketones; in particular: hydrofluoro monoketones, perfluoro monoketones, perfluoro monoketones comprising at least 5 carbon atoms, and mixtures thereof;

fluoroolefins; in particular: perfluoroolefines, hydrofluoroolefins (HFO), hydrofluoroolefins (HFO) comprising at least three carbon atoms, hydrofluoroolefins (HFO) comprising exactly three carbon atoms, trans-1,3,3,3-tetrafluoro-1-propene (HFO-1234ze), 2,3,3,3-tetrafluoro-1-propene (HFO-1234yf), and mixtures thereof; and

- mixtures thereof.

14. The furnace (10) of any one of the preceding claims, wherein the monitoring system (12), in particular the sensor (122), comprises a protective cover that separates the monitoring device (12), in particular the sensor (122), from a surrounding region inside the furnace (10) or outside the furnace (10) and that is permeable to the cover gas (136) and is impermeable to particles, in particular the protective cover being in the form of a protective cover plate or protective cover tube.

15. The furnace (10) of claim 14, wherein the protective cover is selected from at least one of the group consisting of:

* a sintered material,
* a porous material, in particular a porous metal,
* a gauze,
* a mesh,
* a membrane, in particular comprising a polymer material, and
* combinations thereof.

16. The furnace (10) of any one of the preceding claims, wherein the monitoring system (12), in particular the sensor (122), comprises an optical measurement beam at a first wavelength, and an optical reference beam at a second wavelength that is not absorbed by the passivation fluid, in particular fluoroketone.

17. A method of controlling a furnace (10) for melting non-iron metals or non-iron alloys, particularly magnesium or aluminum and their alloys, comprising a step (22) of monitoring in-situ a concentration of a passivation fluid in a cover gas (136) by determining a concentration-dependent electromagnetic property of passivation fluid molecules at at least one wavelength or wavelength band of the electromagnetic wave spectrum.

18. The method of claim 17, wherein the determining the concentration-dependent electromagnetic property comprises determining an emission and/or an absorption and/or a transmission and/or a scattering by the passivation fluid molecules.

19. The method of any one of the claims 17 to 18, further comprising a step (24) of delivering the cover gas (136) to the furnace (10) by controlling a supply (132) of the passivation fluid.

20. The method of claim 19, wherein the step (24) of delivering the cover gas (136) to the furnace (10) comprises the step of injecting the passivation fluid or the passivation fluid mixed with a carrier gas into the furnace (10), in particular into a head space of the furnace (10), using at least one nozzle (135).

21. The method of any one of the claims 17 to 20, wherein the supply (132) of the passivation fluid and/or the at least one nozzle (135) is or are operated as a function of the in-situ measurements of the concentration of the passivation fluid, in particular as a function of a determined emission light power and/or absorption light power of the passivation fluid molecules at the at least one wavelength or wavelength band of the electromagnetic wave spectrum.

22. The method of any one of the claims 17 to 21, wherein the passivation fluid is an organic fluorine compound, in particular a perfluoroketone and/or a fluoroketone comprising from 5 to 9 carbon atoms.

23. The method of any one of the claims 17 to 22, comprising the method element of selecting a passivation fluid to comprises at least one component selected from the group consisting of:

partially or fully fluorinated ethers; in particular: hydrofluoroethers, hydrofluoro monoethers, hydrofluoro monoethers containing at least 3 carbon atoms, perfluoro monoethers, perfluoro monoethers containing at least 4 carbon atoms, fluorooxiranes, perfluorooxiranes, hydrofluorooxiranes, perfluorooxiranes comprising from three to fifteen carbon atoms, hydrofluorooxiranes comprising from three to fifteen carbon atoms, and mixtures thereof;

- partially or fully fluorinated ketones; in particular: hydrofluoro monoketones, perfluoro monoketones, perfluoro monoketones comprising at least 5 carbon atoms, and mixtures thereof;

fluoroolefins; in particular: perfluoroolefines, hydrofluoroolefins (HFO), hydrofluoroolefins (HFO) comprising at least three carbon atoms, hydrofluoroolefins (HFO) comprising exactly three carbon atoms, trans-1,3,3,3-tetrafluoro-1-propene (HFO-1234ze), 2,3,3,3-tetrafluoro-1-propene (HFO-1234yf), and mixtures thereof; and

- mixtures thereof.

24. The method of any one of the claims 17 to 23, comprising the method elements of:

measuring the concentration of the passivation fluid at a first wavelength, and

correcting the measurement by using a second wavelength that is not absorbed by the passivation fluid, in particular fluoroketone.

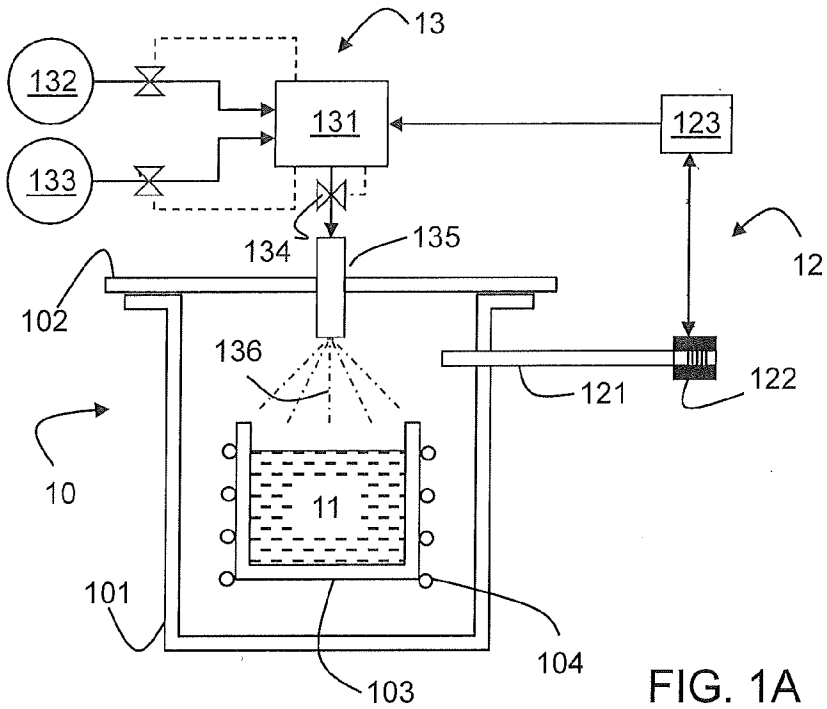

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FIG. 1A

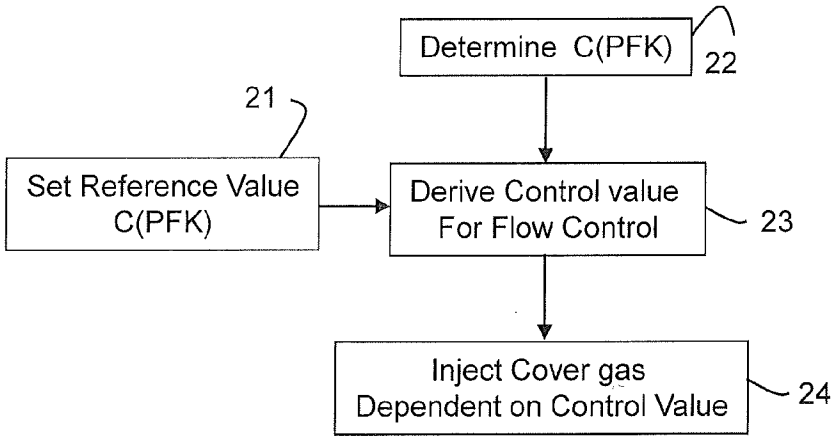

Determine C(PFK)
22
21
Set Reference Value
C(PFK)
Derive Control value
For Flow Control
23
Inject Cover gas
Dependent on Control Value
24

FIG. 2

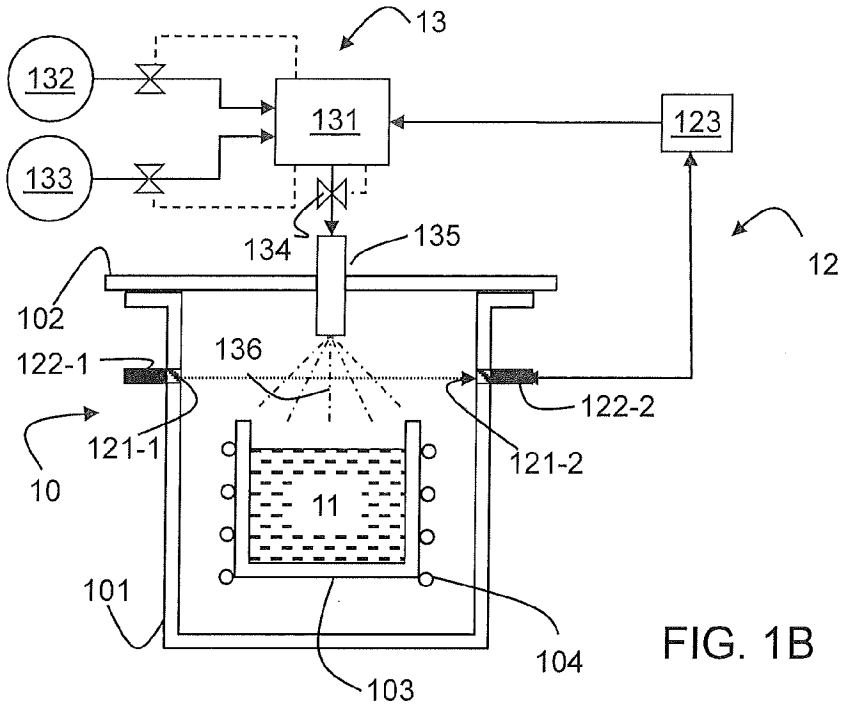

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132
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136
122-1
122-2
121-1
121-2
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FIG. 1B

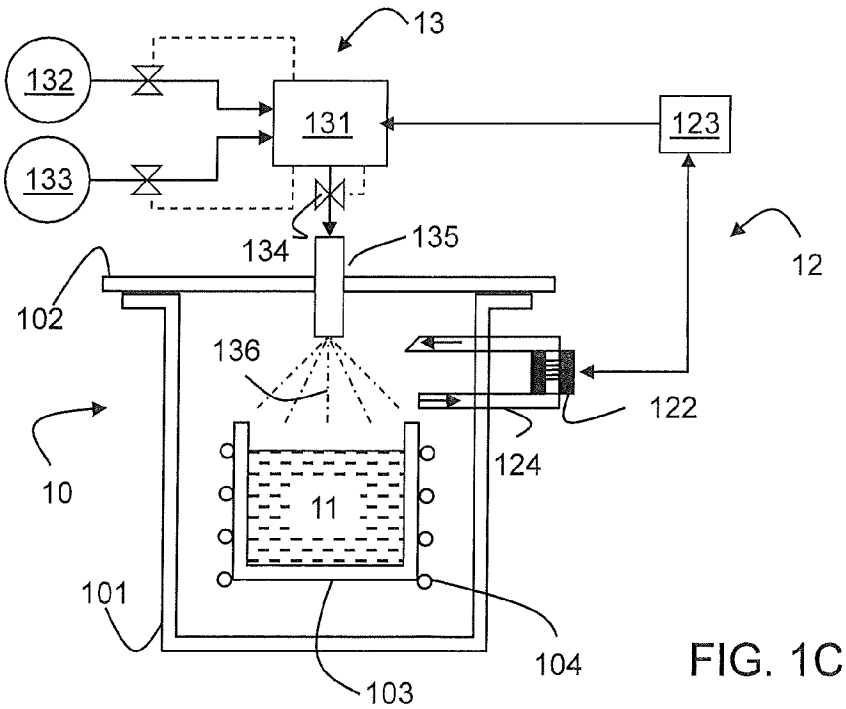

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123
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135
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136
122
124
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101
104
103

FIG. 1C

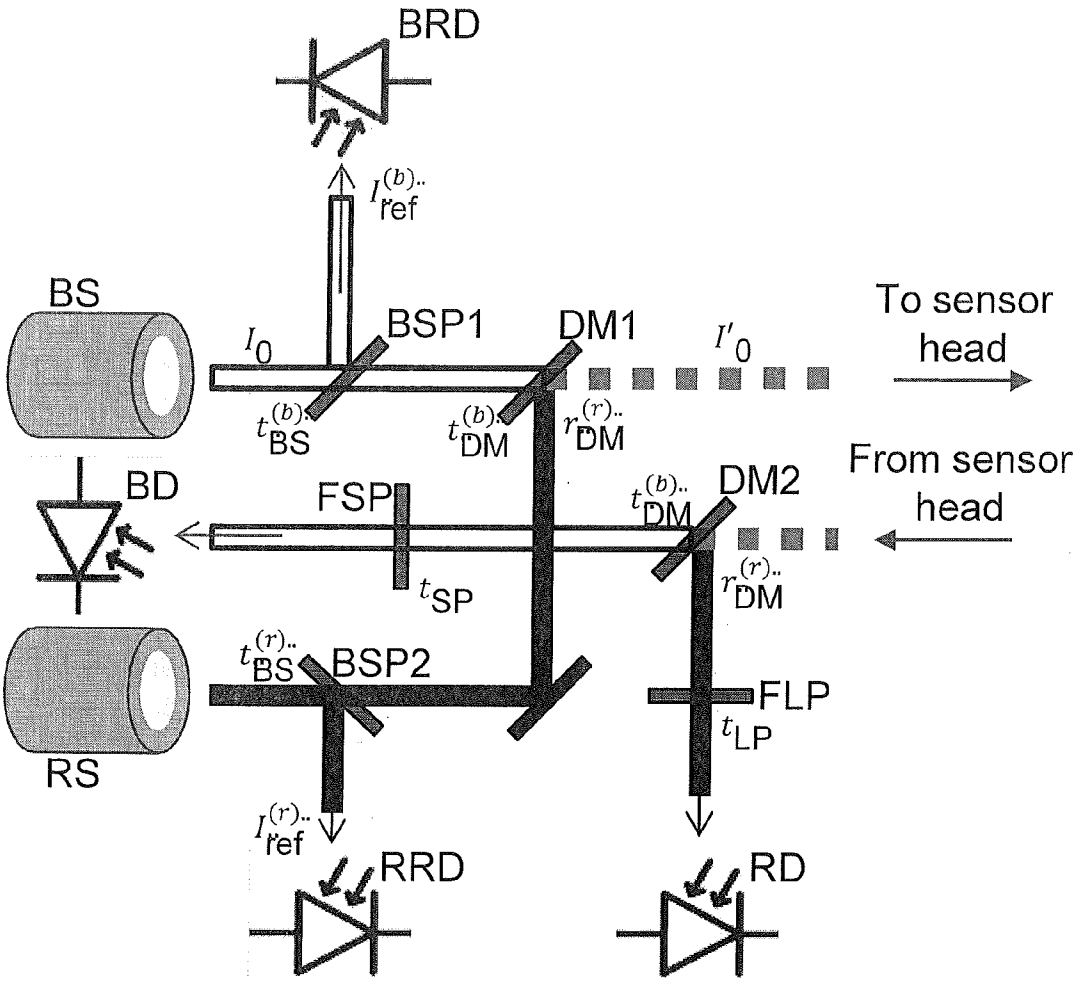

BRD
$I_{ref}^{(b)..}$
BS
I_0
BSP1
DM1
I'_0
To sensor head
$t_{BS}^{(b)..}$
$t_{DM}^{(b)..}$
$r_{DM}^{(r)..}$
From sensor head
BD
FSP
$t_{DM}^{(b)..}$
DM2
t_{SP}
$r_{DM}^{(r)..}$
$t_{BS}^{(r)..}$
BSP2
FLP
t_{LP}
RS
$I_{ref}^{(r)..}$
RRD
RD

Fig. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/068282

A. CLASSIFICATION OF SUBJECT MATTER
INV. F27D7/02 B22D21/00 C22B9/05 C22B26/22 F27D7/06
ADD.

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)
F27D B22D C22B G01J C21B G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

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[X] Further documents are listed in the continuation of Box C.

[X] 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

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 February 2014	17/02/2014

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Gavriliu, Alexandru

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/068282

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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