**Title**

Method of regulating a high temperature gaseous phase process and use of said method

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**Related Art**

US 5060572  
US 5807750  
EP 803725
METHOD OF REGULATING A HIGH TEMPERATURE GASEOUS PHASE PROCESS AND USE OF SAID METHOD

A METHOD FOR THE REGULATION OF A HIGH TEMPERATURE GAS PHASE PROCESS AND THE USE OF THE METHOD

The invention relates to a method for regulating a high temperature gas phase process, in particular CVD, LPCVD (Low Pressure Chemical Vapour Deposition) or CVI, on the basis of measurement curves, determined by infrared spectroscopy, which have at least one spectral region (peak) characteristic for the regulation of the process and differing from the background of the measurement curve.

Usually, chemical compounds have highly specific infrared spectra which are more finely structured than spectra in the visible or ultraviolet regions. Consequently, infrared spectra frequently serve to assist the qualitative analysis in the identification of chemical compounds, whereby a measured spectrum, which contains the chemical compounds of interest, is compared with a so-called reference spectrum and, by quotient formation/division of the spectra, further absorption spectra are obtained which enable identification of the chemical compounds under examination.

As the spectral regions, which are characteristic for the chemical compounds, i.e. peaks, vary substantially in dependence on temperature, it is necessary that, for each temperature at which a process is carried out, a reference curve is determined. The same holds true when infrared spectra have to be measured and evaluated in different installations.

From US 5,175,017 or JP 07-90593A or JP 03-193863A, process regulation by means of EDV evaluation of spectrometer values is known. An overview of the process regulation possibilities, which also include the spectroscopy, can be obtained from the United States Journal of Vacuum Science Technology B13(4) July/August 1995, 1917-1923. US 4,148,931 proposes a process regulation by IR spectroscopy in exhaust gas.

The description of the prior art is not intended to be, nor should it be interpreted as, an indication of the common general knowledge pertaining to the invention, but rather to assist the person skilled in the art in understanding the developmental process which lead to the invention.
From US 5,060,572 there is known a method for regulating a drying process of a printed material strip. In a drying device, there is provided an infrared radiation path for determining concentrations of gas vapours by means of an extension process. This occurs on the basis of a measurement curve obtained by infrared spectroscopy, which has a characteristic spectral range for regulating the process. For regulating the process it is proposed, on one hand, to compare the measurement curve with an intensity of a substantially constant value or to use a reference line which extends as a basis line through points with maximum transmission grade. The taking into account of hardly apparent characteristic spectral ranges (peaks) of the determined measurement curve is not disclosed by the process according to US 5,060,572.

EP 0 549 207 A 1 relates to a device and a method for controlling the formation of large surface diamond films using a heated fire-resistant material such as, for example, graphite or carbon, which is shaped in the form of rods, gratings or baskets. From EP 0 549 207 A 1, the use of graphite for emission of IR radiation is known.

US 5,807,750 relates to an analysis apparatus for optical analysis of substances and discloses the measurement of IR radiation in an exhaust gas passage.

Finally, in EP 0 764 457 A 2 there is described a device and a method for preventing the formation of dioxins in exhaust gases of a refuse incineration installation.

The present invention is based on the problem of developing a method of the first-mentioned type in such a way that with infrared spectroscopy, high temperature gas phase processes, especially CVD, LPCVD and CVI processes, can be optimally and quickly regulated even while temperatures vary during the processes, in such a manner that the gas phase processes are optimized or the accumulation of, in particular, dangerous chemical compounds in the exhaust gas is reduced.
According to the invention, the problem is solved essentially in that for each characteristic spectral range (peak) a straight line (synthetic background) is calculated directly from the measurement curve on the basis of initial and end values of the peak, and in that the regulation of the process takes place by integration of the peak over the straight line or by determining the maximum height of the peak above the straight line or on the basis of another characteristic value of the peak relative to the straight line.

It is thereby in particular provided that the measurement curve is smoothed out, i.e. the background noise is strongly minimized, before the calculation of the straight line. The smoothing can be effected in accordance with the formula established by Kimitz

$$A_i = \frac{1}{16}(A_{i-3} + 4A_{i-1} + 6A_0 + 4A_{i+1} + A_{i+3})$$

where $A_i$ represents the value to be smoothed (i.e. in the present case the peak) and $A_{i+3}$ or $A_{i-3}$ the value before or after the value $A_i$.

By the teachings of the invention, the infrared spectrum can be continuously established and evaluated independently of a spectral background which varies with temperature, so that a regulation of the process is possible while avoiding a reference spectrum at each temperature to be measured. Consequently, immediately after the calculation of the straight line, which is equivalent to a synthetic background, relevant parameters of the process can be regulated on the basis of characteristic values obtained between the straight line and the peak. These include the pressure in a reaction vessel, the gas speed of the process gas, the concentration thereof and/or the temperature in the reaction chamber.
On the basis of the teachings of the invention, it is no longer necessary, after reinstallation, on transferring to other process installations and in particular other or varying temperatures to determine so-called background data banks for the different temperatures before the actual measurements in order to divide the actually measured measurement curves by reference curves thus obtained. Consequently, without any adaptation, the gas composition can be determined even while a process is taking place. This is in particular the case when the positions of the characteristic spectral ranges, i.e. the leading peaks, are known, so that consequently, independent of parameters and also independent of the high temperature gas phase processes to be carried out, an immediate calculation and therewith regulation of the process can occur. In this way, PyC or CVD, LPCVD or CVI installations, e.g. for PyC or SiC coatings, can be optimized or controlled in a problem-free manner.

The method according to the invention can be used, in particular, for regulating a waste, such as a refuse, incineration process, a spectral range of the measurement curve characteristic for an environmentally dangerous gas such as dioxin being the basis for regulating values.

In a CVD process (Chemical Vapour Deposition) for surface coating of e.g. carbon or graphite material with silicon carbide, characteristic peaks measured in the exhaust gas flow, such as HCl and/or CH₄ and/or CH₂SiCl₃ and/or HSiCl₂ and/or SiCl₄ can preferably be the basis for the regulating values.

For determining the measurement curve, IR radiation emitted from an element such as graphite plate in a reaction container, can be measured, the IR radiation, in particular, emitted through an exhaust gas flow from the reaction vessel being the basis. In this way, by adjustment of the process parameters, it can be ensured that e.g. the amount of polychlorosilanes in the exhaust gas is reduced to such an extent that expensive subsequent treatments are avoided. Also, the separating apparatus can be regulated so that, consequently, the CVD process is optimized by means of the method according to
the invention. The same holds true with respect to the optimization of CVI (Chemical Vapour Infiltration) processes and pyrographite coatings (PyC).

The method according to the invention is not, however, restricted to infrared measurements in which the radiation is emitted from a body. Moreover, all known infrared spectroscopy methods employing emission, transmission or reflection spectra can be used.

Further details, advantages and features of the invention appear not only from the claims, from the features to be obtained therefrom - individually and/or in combination - but also from the following description of the preferred embodiments shown in the drawings.

In the drawings:-

Figure 1 shows a single beam/infrared measurement curve,

Figure 2 shows a measurement curve with a synthetic background,

Figure 3 shows an absorption spectrum calculated from the measurement curve of Figure 2, on the basis of a synthetic background,

Figure 4 shows variations of absorption lines in dependence on temperature in a CVD process for coating carbon or graphite material with SiC,

Figure 5 shows a section of a reaction vessel, and

Figure 6 shows a block diagram.

To coat e.g. carbon or graphite material with silicon carbide (SiC), a thermal CVD (Chemical Vapour Deposition) method can be used, e.g. SiHCl₃ or SiCl₄ being reduced in an H₂ atmosphere at 900°C to 1350°C in a reaction chamber and forming a SiC layer
by precipitation onto a substrate. Also, trichlorosilane CH$_3$SiCl$_3$ (MTS) or SiH$_4$ and methane CH$_4$ can be employed instead of MTS. In this respect, however, long-known CVD methods for SiC coating are referred to.

A measurement curve obtained by FTIR (Fourier Transformation IR Spectrometry) measurement is shown in Figure 1. The intensity is there plotted against the wave number cm$^{-1}$. Obviously, the wave number can be replaced by the wavelength or the frequency.

From the measurement curve of Figure 1, it can be seen that this characteristic spectral range includes so-called peaks, which are characteristic for certain chemical compounds. The position of these peaks is known, so that on the basis of the alteration thereof the CVD process can be regulated. According to the state of the art, furthermore, the measurement curves measured at a certain temperature are compared with a reference curve at the same temperature, at which the CVD process is not taking place. From the quotient of the curves, characteristic values of the peaks are obtained in order to be able to reach conclusions with respect to the process.

If the temperature varies during a process, for each temperature then it is necessary to compare a separate reference curve, a so-called background curve, with the actually measured measurement curve, so that consequently an extensive background data bank must be available. Also, when changing installations it is necessary to have corresponding characteristic background, i.e. reference, curves available.

In Figure 4, there is illustrated, by way of example, the variation of characteristic peaks, in a CVD method for coating carbon or graphite with SiC, for the chemical compounds HCl, Cl$_4$, methyltrichlorosilane (MTS), HSiCl$_3$, SiCl$_2$ and SiCl$_4$. It is known that e.g. the peak which is characteristic for HCl decreases as the temperature increases ($T_1<T_2<T_3<T_4$), while the intensity increases for SiCl$_2$. 
According to the invention, it is provided that it is no longer necessary to perform special background measurements, and thus to store reference curves, in order to compare with the actual measurement curves. Furthermore, a so-called synthetic background is calculated from the actually measured measurement curves and this can be used for determining a characteristic value of the spectral range to be examined, i.e. based on the peaks, in order to obtain absorption spectra which can be used for direct regulation of the process.

Thus, in Figure 2 there is shown an experimentally measured measurement curve 10, the intensity being plotted relative to the wave number. The measurement curve 10 includes two characteristic peaks 12 and 14, which are to be used for controlling or regulating the process. For this purpose, before and after the respective peak 12, 14, measurement points 20, 22, 24, 26, preferably six measurement points, are taken into account, at which a straight line 16, 18 is calculated which, in turn, is equivalent to a synthetic background, thus corresponds to a background of a reference measurement which, at the temperature of the corresponding installation on which the measurement curve of Figure 2 is based, would be taken and stored.

From the quotients between the straight lines 16, 18 and the peaks 12, 14, an absorption spectrum is then calculated, which is shown in Figure 3. In this figure, the heights of the peaks 12, 14 shown in Figure 2 are plotted against the wave numbers. From the absorption peaks 12, 14, a process regulation can then follow, the peak of the SiCl₄ (silicon chloride) being used e.g. in the coating of carbon or graphite with SiC as the characteristic peak and thus, in such a way that minimal values remain in an exhaust gas flow.

Before the calculation of the synthetic background, represented by the lines 16, 18, the measurement curve 10 can be smoothed and, more particularly, following the formula

\[ A_i = \frac{1}{16}(A_{i-2} + 4A_{i-1} + 6A_{i} + 4A_{i+1} + A_{i+2}) \]
Ai being the value to be smoothed, and thus the value of the peaks 12, 14, and A_{i\pm x} or A_{i+x} the individual measurement values 20, 22, 24 and 26 directly before and after the value to be smoothed. Preferably, three values before and three values after each value to be smoothed are used, as indicated in Figure 2, by way of example, by reference numerals 20, 22 or 24, 26.

A prerequisite for this process is, of course, that the peaks obtained from the measurement curve 10 are associated unambiguously with certain chemical compounds. If the corresponding spectral ranges, referred as lead peaks, are known, a direct regulation of the process from the lead peaks to be evaluated can follow independently of the installation in use. In this way, PyC or CVD, LPCVD or CVI installations, e.g. for PyC or SiC coating, can be optimized or controlled in a problem-free manner.

In Figure 5, there is shown in section a reaction chamber 28 in which a substrate of carbon or graphite is to be coated with SiC. For this purpose, the reaction chamber 28 is adjusted to a temperature T of e.g. 1300°C at a pressure of e.g. <13.33 x 10³ Pa. In addition, desired amounts of silane, such as methyltrichlorosilane, and hydrogen are introduced into the reaction chamber 28 in order to coat SiC on the graphite or carbon substrate.

To determine the coating of silane on the substrate and also the formation of silicon carbide or the proportion of explosive polychlorosilane in the exhaust gas, there is located beneath an exhaust gas pipe 30 a body, such as graphite plate 32, which assumes the temperature of the reaction chamber, the IR radiation emitted by this body through the exhaust gas pipe 30 being measured by an FTIR spectrometer 34. Following the measurement curve, according to the method of the invention, a synthetic background in the vicinity of the characteristic peaks 12, 14 is then obtained in order to then calculate absorption spectra according to Figure 3 and, from these, to control the process. Obviously, values for regulating the process can be deduced from the measurement curve itself after calculating the lines 16, 18.
Therefore, by the method according the invention, peaks 12, 14 are consequently "cut out" from the measurement curve 10, and straight lines are obtained from the initial and end values 20, 22, 24, 26 of the peaks 12, 14, so that with the help thereof the theoretical background in the region of the peaks 12, 14 is calculated. By quotient formation between the synthetic background 16, 18 and the experimentally determined peaks 12, 14, peak heights or peak areas are then determined. Also, for each peak a respective background is calculated, only the actually measured values present immediately at the beginning and the end of the peaks 12, 14 being used for determining the straight lines 16, 18.

By the method according to the invention, a continuous obtaining and evaluation of infrared spectra is possible independently of a spectral background which varies with temperature. Consequently, on the basis of the experimentally actually measured spectrum, regulation of the process itself is possible. In direct dependence on the values deduced, which equal an on-line evaluation, all relevant parameters such as the vessel pressure, gas speed, concentration of the process gases and temperature can then be regulated and controlled.

The teachings of the present invention make it possible that after reassembly or on change of installations or alteration of temperatures, the background data banks required according to the state of the art and which must be available before the actual measurements, do not have to be available. Without any adaptation, while the process is taking place, such as coating, the gas composition can be determined and the process can thereby be controlled.

It is noted that the method according to the invention can be utilized for all, in particular, high temperature gas phase processes, and thus also in CVI (Chemical Vapour Infiltration) processes such as pyrographite coating, an optimal precipitation rate being ensured without altering the structure of the pyrographite. Consequently, on the basis of the teachings of the invention, it is made possible, in a problem-free manner, to control
on-line processes for handling high temperature heat exchanger probes, reproduceable results being achievable.

The method according to the invention can, however, also be utilized in other fields, in particular in the field of waste, such as refuse, incineration. Thus, on the basis of the teachings of the invention, the spectral ranges can be observed which correspond to environmentally dangerous gases such as dioxin, in order to control the process on the basis of the extension of the peaks, and thus e.g. to raise the temperature, when on the basis of the peak the proportion of dioxin is evaluated as being impermissible.

In Figure 6 there is shown block diagram. With an FTIR spectrometer 34, an infrared spectrum with peaks, characteristic for a reaction chamber 36, is determined, in order to determine, in an evaluation unit 38, a synthetic background by calculating a straight line from measurement values located before and beyond the respective peak. From the calculated characteristic values between the respective straight lines and peaks, such as areas (integral) or peak heights, process parameters in the reaction chamber 34 are regulated by means of a control/regulation unit 40. In addition, by the control/regulation unit 40, units indicated by reference numeral 42 for changing the temperature in the reaction chamber 36, the pressure in the reaction chamber 36 or the proportion of the process gases can be controlled.
1. A method for the regulation of a high temperature gas phase process, especially CVD, LPCVD or CVI, on the basis of measurement curves, determined by infra-red spectroscopy, which have at least one spectral region (peak) characteristic for the regulation of the process and differing from the background of the measurement curve, wherein for each characteristic spectral range (peak) a straight line (synthetic background) is calculated directly from the measurement curve on the basis of initial and end values of the peak, and in that the regulation of the process takes place by integration of the peak over the straight line or by determining the maximum height of the peak above the straight line or on the basis of another characteristic value of the peak relative to the straight line.

2. A method according to claim 1, wherein the regulation of the process takes place by continuous establishment and evaluation of measurement curves.

3. A method according to claim 1 or 2, wherein an on-line evaluation of the peak or peaks is effected for adjustment of process parameters.

4. A method according to claim 3, wherein the process parameters are pressure, temperature, speed or concentration of process gases.

5. A method according to any one of the preceding claims, wherein the evaluation of the measurement curve takes place without being based on a reference measurement at a temperature which corresponds to that of the process to be regulated.

6. A method according to any one of the preceding claims, wherein the X initial values and the Y end values of a peak are used for calculation of the straight line.

7. A method according to claim 6, wherein X is equal to Y.
8. A method according to claim 6 or 7, wherein 5 to 7 initial values and 5 to 7 end values of the peak are used as a basis for the calculation of the straight line.

9. A method according to claim 6 or 7, wherein 6 initial values of the peak are used as a basis for the calculation.

10. A method according to any one of claims 6 to 8, wherein 6 end values of the peak are used as a basis for the calculation.

11. A method according to at least one of the preceding claims, wherein the measurement curve is determined by IR radiation emitted from an element present in a reaction chamber.

12. A method according to claim 11, wherein the element is a graphite plate.

13. A method according to claim 11 or 12, wherein the IR radiation of the element, emitted through an exhaust channel of the radiation chamber, is measured.

14. Application of the method according to any one of claims 1 to 13 for regulating a CVD process for surface coating of carbon or graphite material with SiC, at least one peak, preferably measured in the exhaust gas stream, characteristic for HCl and/or CH₄ and/or CH₃SiCl₂ and/or HSiCl₃ and/or SiCl₄ is used as a basis for regulating values.

15. Application of the method according to at least one of claims 1 to 13 for regulating a waste or refuse incineration process, at least one peak, which is characteristic of an environmentally dangerous gas such as dioxin, of the measurement curve being used as a basis for the regulating values.
16. A method for the regulation of a high temperature gas phase process substantially as hereinbefore described with reference to the accompanying drawings.

17. Application of the method according to claim 14 substantially as hereinbefore described with reference to the accompanying drawings.

18. Application of the method according to claim 15 substantially as hereinbefore described with reference to the accompanying drawings.

Dated this 30th day of June 2003

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