

Description

BACKGROUND OF THE INVENTION

The present invention relates to a spectroscopic analyzing method and system in which the ingredients of the sample are quantitatively analyzed with being classified by the conditions in the sample.

In the controlling the quality of the metal during smelting, it is necessary to analyze the ingredients of the metal with classifying the conditions in the sample.

The conditions of the ingredients in the sample can be classified into two. One is the composite conditions such as nitrogen, oxide, and sulfide etc.

The other is the conditions of an alloy in which the elements are dispersed in a metal.

To analyze the ingredient elements depending on the classification of the composite conditions and the alloy conditions, there are conventionally chemical methods for separately analyzing using various solution methods.

However, they are not so speedy that they can be effectively applied to controlling during smelting.

The quality control during smelting the metal is then difficult.

EP-A-0 009 766 discloses an apparatus for emission spectrochemical analysis, in which emission lines characteristic of the elements of a sample are measured spectrometrically.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a speedy quantitative analysis of the ingredients in a sample with being classified by the condition of the ingredients in the sample, using a spectroscopic analysis, so that the quality control during smelting the metal is easily done.

Briefly described, in accordance with the present invention, the quantitative analysis of the ingredients in a sample with being classified by the conditions in the sample is done with a spectroscopic analysis. For this purpose, the sample is excited a great number of times to emit. Each time the sample emits, the light intensity of the lines regarding the ingredient elements and the non-ingredient elements is detected to store the detected light intensity data of the lines. The light emission containing the ingredient elements and the non-ingredient elements over a predetermined level is specified.

Then, it is determined that there is present a composition of the ingredient element and the non-ingredient element in a region of the sample corresponding to the specified emission. According to the present invention, speedy quantitative analysis of the ingredients in the sample with being clas-

sified by the conditions in the sample is made by the spectroscopic analysis. For example, the diameter of a spark region of a single pulse by the spark discharge spectroscopic analysis is about 30 μ .

The element in a metal for composing a non-metal composition such as an oxide is generally present as an alloy component partially and another part of the element is formed as an oxide or a nitride.

These non-metal compositions are deposited as an interference material in the crystal boundary of the metal. Although the size of the interference material may be different from depending on its kind, the metal of Al or Ca in the steel is melted into Fe and the oxide is Al_2O_3 and CaO, which are dispersed as the interference material with the size of about 5 μ .

Therefore, the intensity of the spectra of Al and Ca given by each of the single spark is greatly changed on the conditions whether the discharge diameter can compass an oxide, or not and how the size of the oxide is. This is because the melting elements of Al are dispersed in the metal in a small degree and if there is no interference material in the spark region, the ratio of Al in the spark region is small so that the light intensity of the line of Al is low and the change of the light intensity of the line per spark is also small. However, if there is an interference material in the spark region, Al is gathered to the interference material and the ratio of Al in the spark region is great to provide strong light intensity of the line of Al. The change of the light intensity is proportional to the amount of the interference material. The change of the given spectra intensity is several times to several hundred times. If there is an oxide of Al, the line due to oxygen appears of course.

Therefore, if the line due to oxygen is detected in a spark, it is assumed that the spark is generated from a region containing an oxide of the ingredients of the sample, and it is determined whether the light intensity of line of the ingredient elements of Al or Ca or the like show intensity more than the average intensity of each of the elements in a great number of discharges. For example, if the light intensity of the line of Al is in average and the light intensity of the line of Ca shows a predetermined value more than the average intensity, it can be determined that the oxide of Ca, CaO is contained in the spark region. On the contrary, if the light intensity of the line of Al shows a predetermined value more than the average intensity and the light intensity of the line of Ca is in average, it can be determined that both Al_2O_3 is contained in the spark region. If the light intensity of the line of Al and Ca is more than the average, it can be determined that both Al_2O_3 and CaO are contained in the spark region.

This can be applied to oxides and nitrides of Mg, Si, Ti, B and Zr, and metal compositions such as TiC etc.

The above described analysis can be made using spark by excitement due to laser beam. The laser beam can provide high analysis accuracy and two-dimension map showing the conditions of the ingredients in the sample.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will become more fully understood from the detailed description given hereinbelow and the accompanying drawings which are given by way of illustration only, and thus are not limitative of the present invention and wherein:

FIG. 1 is a block diagram of a spectroscopic analyzing system of the present invention in a preferred embodiment;

FIG. 2 is data given by the spectroscopic analyzing system of FIG. 1; and

FIG. 3 is a block diagram of a spectroscopic analyzing system in another preferred embodiment of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

FIG. 1 shows a block diagram of an analyzing system according to the present invention. A spark chamber 1 is provided for sparking a specimen 3. The spark chamber 1 is full of argon gas as an inert gas. A spark circuit 2 is operated to generate high voltage pulses for sparking. A high voltage pulse is applied between a facing electrode and the specimen 3 from the spark circuit 2 so that a spark discharge is enabled between the facing electrode 4 and the specimen 3. A spectrophotometer 5 is provided whose contents are vacuum. An inlet slit 6 is used to take on parallel radiation from the spark light generated between the facing electrode 4 and the specimen 3. The parallel radiation is directed to some predetermined direction. A diffraction grating 7 is provided for providing spectroscopic analysis of the spark light from the inlet slit 6. Outlet slits 8 through 11 are positioned on the spectra image picture and the line position of each of the elements. Then, the spark passing through each of the outlet slits 8 through 11 only is incident on photomultipliers 12 through 15. Single pulse integrators 16 through 19 are provided for into grating light intensity signal of the line detected by the photomultipliers 12 through 15 at the unit of each spark. Thus, a detection means comprises the photomultipliers 12 through 15 and the single pulse integrators 16 through 19. A switch 20 is provided for subsequently forwarding the integration value (simple data), integrated by the integrators 16

through 19 to an analog/digital (A/D) converter 21. The A/D converter 21 is operated to transfer the received simple data to digital signals. A memory 22 is provided for storing the simple data subsequently in a predetermined area per element and storing the other data in another area. A microcomputer 23 is operated to control the respective elements and calculate the various data, which serves as the specifying means, the detection means and the prepare means of the present invention.

In operation, when the spark circuit generated high voltage pulses to the facing electrode 4, the spark discharges between the specimen 3 and the facing electrode 4 are repeated at one thousand to several thousands times to measure the light intensity for each of the elements at each spark as shown in FIG. 2 (A) to 2 (D). In these figures, the length of the vertical bar at a position, at which the spark order of each of the elements is the same, corresponds to the output signal of each of the single pulse integrators 16 through 19. The length of the vertical bar in each of the graphs at the same position indicates the light intensity of the line at one spark. The given light intensity data of the line of each of the elements are subsequently stored into the memory 22. From the data stored in the memory 22, the light intensity of the line per spark of the elements (O, Al, Ca, Mg etc.) is calculated into a percentage of the contents. The percentage of the contents is preliminarily determined in a detection line prepared by a reference sample with little interference material. Calculating into the percentage of the contents enables analysis data with deleting a background. Thus, the average and a dispersion value of the percentage of the contents of each of the elements per spark are determined, so that a composition detection level is set from the dispersion condition of the data. For example, the detection level is such that, assuming that the average content is $+3\sigma$, some element provides data more than it at a spark, it is determined that the spark region of that spark contains a composition or an interference material of that element.

FIG. 2 (A) shows the light intensity of the line of oxygen. Concerning the spark over the detection level S, it is assumed that an oxide may be present and in the same spark, the data of the other elements of Al, Ca, Mg etc. are checked to look for the element over the detection level. If there is a spark over the detection level, it can be assumed that an oxide of that element is contained in that spark. The sparks marked with a circle in FIGs. 2 (B) to 2 (D) are determined to contain an oxide of the element (Al_2O_3 for Al, CaO for Ca, and MgO for Mg). As shown in FIG. 2 (A), the reason why the emission of the line of the oxygen is detected at each spark is that the oxygen resolved into the

metal is added to a simple backlight. Such a low level light intensity does not indicate the presence of an oxide. Of course, in principal, if the light intensity of the line of a metal element is over the predetermined level and there is the line of the oxygen, the oxide of that metal element can be considered to be present.

In a spark whose region is assumed to contain an oxide, it is explained how to calculate the percentage of the content, Z% of the oxide of an oxidized element (for example, Al) in the spark region. At first, the content amount of the oxidized element in the spark is determined from a detection line, so that the content amount in the spark region of that spark is A%. The average content of that element over the sample is B%. The gravity of an oxide of that element/the gravity of that element = C. Then,

$$Z = (A-B) \times C$$

The contents of the oxide in each of the elements at each of the sparks in which an oxide of an element is specified to be contained are accumulated. The accumulated value is divided by all the spark times of the single analysis to obtain the average value of the oxide of each of the elements. Using that average value, the content of the oxide of each of the elements in the whole of the sample is calculated. The average of the contents of each of the elements in sparks other than the specified sparks is determined. The average is outputted as the content of the simple substance of each element.

FIG. 3 shows a block diagram of the spectroscopic analyzing system in another preferred embodiment of the present invention in which the facing electrode 4 is replaced by a laser gun 30 and the spark circuit 2 is replaced by a laser gun driving circuit 31, a CRT 33 is connected as a display means to the microcomputer 23. The specimen 3 is excited by the laser beam. A two-dimensional map indicating the conditions in the specimen is displayed in the CRT 33. The other parts and the data processing operation are similar as the above embodiment. The suitable laser in this case is N₂ laser beam which is featured by having short laser pulse and providing high output. When the N₂ laser beam is incident on a metal sample under the pressure lower than several torr, the white primary plasma having the small diameter and the secondary plasma which surrounds the white primary plasma in a semispheric form are both generated. The emission of the secondary plasma is used because the emission of the secondary plasma can provide high analysis accuracy without the influence of the background. The emission of the laser beam is expanded over the entire surface of the specimen with scanning. In the

above embodiment using the spark discharge the discharge position of the spark discharge is randomized so that if the discharge position is shifted to a single point, it is impossible to obtain the uniform analysis results over the entire surface of the specimen 3. However, in this preferred embodiment, the emission of the laser beam is carried out with scanning the entire surface of the specimen 3. Here, the average analysis results over the entire surface of the specimen 3 can be assured in this embodiment.

Further, the position information given by scanning the laser beam over the entire surface of the specimen 3 and the analysis results corresponding to the position information are composed to a two-dimensional map showing the conditions of the elements in the specimen 3. The two-dimensional map is prepared by the microcomputer 23 and displayed by the CRT 33. Then, the conditions of the elements in the specimen are visually understood.

As described above, according to the present invention, speedy quantitative analysis of the ingredients in the specimen with being classified by the conditions of the ingredients in the specimen using the spectroscopic analysis, so that the quality control during smelting the metal is easily done.

While only certain embodiments of the present invention have been described, it will be apparent to those skilled in the art that various changes and modifications may be made therein without departing from the scope of the present invention as claimed.

Claims

1. A spectroscopic analyzing method comprising the steps of;
 - exciting a specimen at a number of times for emission;
 - detecting the light intensity data of a line of an ingredient element of said specimen and of a non-ingredient element of said specimen per emission;
 - storing the detected light intensity data of the line;
 - specifying emission which contains said ingredient element and said non-ingredient element over a predetermined level, based on said stored data; and
 - determining that a composite of the ingredient element and the non-ingredient element is present in a region of said specimen corresponding to said specified emission.
2. The spectroscopic analyzing method as set forth in claim 1, wherein said specifying step comprises a step for calculating the contents

metal is added to a simple backlight. Such a low level light intensity does not indicate the presence of an oxide. Of course, in principal, if the light intensity of the line of a metal element is over the predetermined level and there is the line of the oxygen, the oxide of that metal element can be considered to be present.

In a spark whose region is assumed to contain an oxide, it is explained how to calculate the percentage of the content, Z% of the oxide of an oxidized element (for example, Al) in the spark region. At first, the content amount of the oxidized element in the spark is determined from a detection line, so that the content amount in the spark region of that spark is A%. The average content of that element over the sample is B%. The gravity of an oxide of that element/the gravity of that element = C. Then,

$$Z = (A-B) \times C$$

The contents of the oxide in each of the elements at each of the sparks in which an oxide of an element is specified to be contained are accumulated. The accumulated value is divided by all the spark times of the single analysis to obtain the average value of the oxide of each of the elements. Using that average value, the content of the oxide of each of the elements in the whole of the sample is calculated. The average of the contents of each of the elements in sparks other than the specified sparks is determined. The average is outputted as the content of the simple substance of each element.

FIG. 3 shows a block diagram of the spectroscopic analyzing system in another preferred embodiment of the present invention in which the facing electrode 4 is replaced by a laser gun 30 and the spark circuit 2 is replaced by a laser gun driving circuit 31, a CRT 33 is connected as a display means to the microcomputer 23. The specimen 3 is excited by the laser beam. A two-dimensional map indicating the conditions in the specimen is displayed in the CRT 33. The other parts and the data processing operation are similar as the above embodiment. The suitable laser in this case is N₂ laser beam which is featured by having short laser pulse and providing high output. When the N₂ laser beam is incident on a metal sample under the pressure lower than several torr, the white primary plasma having the small diameter and the secondary plasma which surrounds the white primary plasma in a semispheric form are both generated. The emission of the secondary plasma is used because the emission of the secondary plasma can provide high analysis accuracy without the influence of the background. The emission of the laser beam is expanded over the entire surface of the specimen with scanning. In the

above embodiment using the spark discharge the discharge position of the spark discharge is randomized so that if the discharge position is shifted to a single point, it is impossible to obtain the uniform analysis results over the entire surface of the specimen 3. However, in this preferred embodiment, the emission of the laser beam is carried out with scanning the entire surface of the specimen 3. Here, the average analysis results over the entire surface of the specimen 3 can be assured in this embodiment.

Further, the position information given by scanning the laser beam over the entire surface of the specimen 3 and the analysis results corresponding to the position information are composed to a two-dimensional map showing the conditions of the elements in the specimen 3. The two-dimensional map is prepared by the microcomputer 23 and displayed by the CRT 33. Then, the conditions of the elements in the specimen are visually understood.

As described above, according to the present invention, speedy quantitative analysis of the ingredients in the specimen with being classified by the conditions of the ingredients in the specimen using the spectroscopic analysis, so that the quality control during smelting the metal is easily done.

While only certain embodiments of the present invention have been described, it will be apparent to those skilled in the art that various changes and modifications may be made therein without departing from the scope of the present invention as claimed.

Claims

1. A spectroscopic analyzing method comprising the steps of:
 - exciting a specimen at a number of times for emission;
 - detecting the light intensity data of a line of an ingredient element of said specimen and of a non-ingredient element of said specimen per emission;
 - storing the detected light intensity data of the line;
 - specifying emission which contains said ingredient element and said non-ingredient element over a predetermined level, based on said stored data; and
 - determining that a composite of the ingredient element and the non-ingredient element is present in a region of said specimen corresponding to said specified emission.
2. The spectroscopic analyzing method as set forth in claim 1, wherein said specifying step comprises a step for calculating the contents



of each of said elements based on the light intensity data of the line and for specifying the emission at the level of the contents.

3. The spectroscopic analyzing method as set forth in claim 2, wherein said predetermined level is selected by the average and a dispersion value of the contents per emission. 5
4. The spectroscopic analyzing method as set forth in claim 1, wherein said excitement step comprises a step for discharging said specimen. 10
5. The spectroscopic analyzing method as set forth in claim 1, wherein said excitement step comprises a step for using a laser. 15
6. A spectroscopic analyzing system comprising;
 - excitement means (1, 2, 4) for exciting a specimen (3) for emission, spectroscopic means (5) for making spectroscopic analysis of the emission of said specimen; 20
 - detection means (12-23) for detecting the light intensity of a line at each of said spectroscopic analysis by said spectroscopic means (5) per emission; 25
 - storage means (22) for storing the light intensity data of the line; characterized by
 - specification means (23) for specifying emission in which an ingredient element of said specimen (3) and a non-ingredient element of said specimen are contained over a predetermined level, based on the light intensity data of the detected line; and 30
 - determination means (22, 23) for determining that a composition of the ingredient element and the non-ingredient element is present in a region of said specimen corresponding to said specified emission. 40
7. The spectroscopic analyzing system as set forth in claim 6, wherein said specification means (23) comprises means for calculating the contents of each of said elements based on the light intensity data and for specifying the emission at the level of the contents. 45
8. The spectroscopic analyzing system as set forth in claim 7, wherein said predetermined level is selected by the average and a dispersion value of the contents per emission. 50
9. The spectroscopic analyzing system as set forth in claim 6, wherein said excitement means comprises means for discharging said specimen. 55

10. The spectroscopic analyzing system as set forth in claim 6, wherein said excitement means comprises a laser beam.

11. The spectroscopic analyzing system as set forth in claim 10, further comprising preparation means responsive to the determination of said determination means for preparing a two-dimensional map; and
display means (33) responsive to said preparation means for displaying the two-dimensional map.

Patentansprüche

1. Spektroskopieanalyseverfahren mit folgenden Schritten:
 - mehrfaches Anregen einer Probe so, daß diese emittiert;
 - Erfassen der Lichtintensitätsdaten einer Linie eines Bestandteilelements der Probe und eines Nichtbestandteilelements der Probe pro Emission;
 - Einspeichern der erfaßten Lichtintensitätsdaten für die Linie;
 - Spezifizieren einer Emission, die das Bestandteilelement und das Nichtbestandteilelement über einem vorgegebenen Niveau enthält, auf Grundlage der abgespeicherten Daten; und
 - Bestimmen, daß eine Verbindung aus dem Bestandteilelement und dem Nichtbestandteilelement in einem Bereich der Probe vorhanden ist, der der spezifizierten Emission entspricht.
2. Spektroskopieanalyseverfahren nach Anspruch 1, bei dem der Spezifizierschritt einen Schritt zum Berechnen des Inhalts jedes der Elemente auf Grundlage der Lichtintensitätsdaten der Linie und zum Spezifizieren der Emission mit dem Niveau entsprechend dem Gehalt umfaßt.
3. Spektroskopieanalyseverfahren nach Anspruch 2, bei dem das vorgegebene Niveau durch den Mittelwert und einen Streuungswert für den Gehalt pro Emission ausgewählt ist.
4. Spektroskopieanalyseverfahren nach Anspruch 1, bei dem der Anregungsschritt einen Schritt zum Entladen der Probe umfaßt.
5. Spektroskopieanalyseverfahren nach Anspruch 1, bei dem der Anregungsschritt einen Schritt der Verwendung eines Lasers umfaßt.
6. Spektroskopieanalyzesystem mit:



- einer Anregungseinrichtung (1, 2, 4) zum Anregen einer Probe (3) zur Emission;
 - einer Spektroskopieeinrichtung (5) zum Ausführen einer Spektroskopieanalyse der Emission der Probe;
 - einer Erfassungseinrichtung (12 - 23) zum Erfassen der Lichtintensität einer Linie bei jeder Spektroskopieanalyse durch die Spektroskopieeinrichtung (5) pro Emission;
 - einer Speichereinrichtung (22) zum Einspeichern der Lichtintensitätsdaten für die Linie;
gekennzeichnet durch
 - eine Spezifiziereinrichtung (23) zum Spezifizieren einer Emission, in der ein Bestandteilselement der Probe (3) und ein Nichtbestandteilselement der Probe über einem vorgegebenen Niveau enthalten sind, auf Grundlage der Lichtintensitätsdaten für die erfaßte Linie; und
 - eine Bestimmungseinrichtung (22, 23) zum Bestimmen, daß eine Verbindung aus dem Bestandteilselement und dem Nichtbestandteilselement in einem Bereich der Probe vorhanden ist, der der spezifizierten Emission entspricht.
7. Spektroskopieanalysesystem nach Anspruch 6, bei dem die Spezifiziereinrichtung (23) eine Einrichtung zum Berechnen des Inhalts jedes der Elemente auf Grundlage der Lichtintensitätsdaten und zum Spezifizieren der Emission vom Niveau entsprechend dem Gehalt aufweist.
8. Spektroskopieanalysesystem nach Anspruch 7, bei dem das vorgegebene Niveau durch den Mittelwert und einen Streuungswert für den Gehalt pro Emission ausgewählt ist.
9. Spektroskopieanalysesystem nach Anspruch 6, bei dem die Anregungseinrichtung eine Einrichtung zum Entladen der Probe aufweist.
10. Spektroskopieanalysesystem nach Anspruch 6, bei dem die Anregungseinrichtung einen Laserstrahl aufweist.
11. Spektroskopieanalysesystem nach Anspruch 10, ferner mit
- einer auf die Bestimmung durch die Bestimmungseinrichtung ansprechenden Erstellungseinrichtung zum Erstellen einer zweidimensionalen Karte; und
 - einer Anzeigeeinrichtung (33), die auf die Erstellungseinrichtung reagiert, um die zweidimensionale Karte anzuzeigen.

Revendications

1. Procédé d'analyse spectroscopique, comprenant les étapes consistant à:
 - exciter un échantillon un certain nombre de fois pour une émission;
 - détecter les données d'intensité lumineuse d'une raie d'un élément constitutif dudit échantillon et d'un élément non constitutif dudit échantillon par émission;
 - mémoriser les données détectées d'intensité lumineuse de la raie;
 - spécifier l'émission qui contient ledit élément constitutif et ledit élément non constitutif à un niveau prédéterminé, à partir desdites données mémorisées; et
 - déterminer qu'un composé de l'élément constitutif et de l'élément non constitutif est présent dans une zone dudit échantillon qui correspond à ladite émission spécifiée.
2. Procédé d'analyse spectroscopique selon la revendication 1, dans lequel ladite étape de spécification comprend une étape pour calculer le contenu de chacun desdits éléments à partir des données d'intensité lumineuse de la raie et pour spécifier l'émission au niveau du contenu.
3. Procédé d'analyse spectroscopique selon la revendication 2, dans lequel ledit niveau prédéterminé est choisi par la moyenne et par une valeur de dispersion du contenu par émission.
4. Procédé d'analyse spectroscopique selon la revendication 1, dans lequel ladite étape d'excitation comprend une étape pour décharger ledit échantillon.
5. Procédé d'analyse spectroscopique selon la revendication 1, dans lequel ladite étape d'excitation comprend une étape pour l'utilisation d'un laser.
6. Système d'analyse spectroscopique, comportant
 - un moyen d'excitation (1, 2, 4) pour exciter un échantillon (3) pour une émission, un moyen spectroscopique pour faire (5) une analyse spectroscopique de l'émission dudit échantillon;
 - un moyen de détection (12-23) pour détecter l'intensité lumineuse d'une raie lors de chacune desdites analyses spectroscopiques par ledit moyen spectroscopique (5) par émission;
 - un moyen de mémorisation (22) pour mémoriser les données d'intensité lumineuse de



la raie; caractérisé par

un moyen de spécification (23) pour spécifier l'émission durant laquelle un élément constitutif dudit échantillon (3) et un élément non constitutif dudit échantillon sont contenus à un niveau prédéterminé, en fonction des données d'intensité lumineuse de la raie détectée; et

un moyen de détermination (22, 23) pour déterminer qu'un composé de l'élément constitutif et de l'élément non constitutif est présent dans une zone dudit échantillon correspondant à ladite émission spécifiée.

7. Système d'analyse spectroscopique selon la revendication 6, dans lequel ledit moyen de spécification (23) comprend un moyen pour calculer le contenu de chacun desdits éléments à partir des données d'intensité lumineuse et pour spécifier l'émission au niveau du contenu. 15 20
8. Système d'analyse spectroscopique selon la revendication 7, dans lequel ledit niveau prédéterminé est choisi par la moyenne et par une valeur de dispersion du contenu par émission. 25
9. Système d'analyse spectroscopique selon la revendication 6, dans lequel ledit moyen d'excitation comprend un moyen pour décharger ledit échantillon. 30
10. Système d'analyse spectroscopique selon la revendication 6, dans lequel ledit moyen d'excitation comprend un faisceau laser. 35
11. Système d'analyse spectroscopique selon la revendication 10, comprenant en outre un moyen de préparation réagissant à la détermination dudit moyen de détermination pour préparer une configuration bidimensionnelle; et un moyen de visualisation (33) réagissant audit moyen de préparation pour afficher la configuration bidimensionnelle. 40 45

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