Romanian Reports in Physics, Vol. 62, No. 2, P. 350–359, 2010

CONTROL OF Ca IN STEELS USING SPARK DATA TECHNIQUE

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(Received August 10, 2009)

Abstract. In order to ensure the purity of steel, the control of chemical properties of the steel melt and the content of nonmetallic inclusions is an important factor in designing steel [1, 2]. A good fluidity of steel in continuous casting involves knowing full and rapid content of Al and Ca, the soluble/insoluble part and types of inclusions formed, primarily aluminatul calcium and sulphide calcium.

This paper aims to present a new method of inclusional analysis of steel's purity, with application to spectrochimical method of optical emission – Technique Spark DATA (Device of Treatment and Acquisition) [3]. This measurement technique can rapidly determine the insoluble part to every interested element of steel and a complete analysis of the types of inclusions, the number, size and their distribution in steel. Unlike the other methods of analysis:laser surface hardness [4], RTL study [5], electron spectroscopy, electron microscopy or optical microscopy [6, 7, 8], spectrochemical analysis [9, 10], the technique Spark DATA has the advantage that provides a large amount of information on the purity of steel is fast, the information can be transmitted in real time, surface preparation is minimal, reduced operating costs, and results are sufficiently precise for the purpose.

Key words: optical emission**,** Spark DATA technique, aluminium, calcium.

1. PRINCIPLE OF MEASUREMENT OES – SPARK DATA

The novelty in Spark DATA technique in optical emission spectrometry with glitter, consists in the acquisition of data on spectral intensities. In the classic way, the intensity measured for a chemical element represents an integration, a sum of all intensities obtained from the basic data sparks during the flash [1, 2, 3].

In this technique spectral intensities emitted by the sample at each flash of discharge are measured and stored for up to 32 measurement channels. The result is a diagram of a flash, with number of sparks on the *X* axis and intensity measured on the axis *Y*. Figure 1 presents a diagram for aluminum shaft in steel.

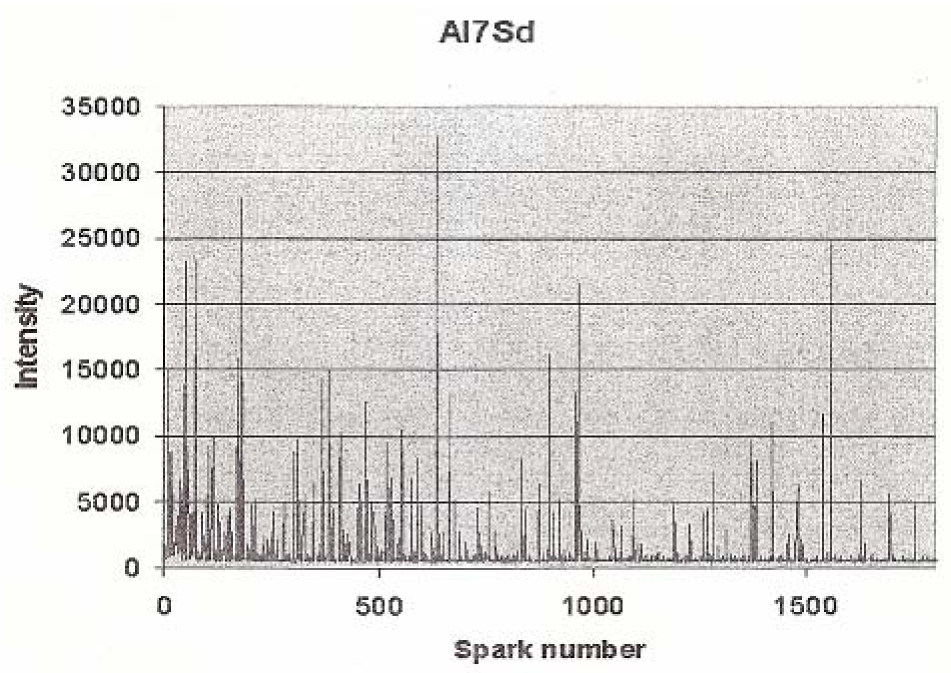

Fig.1 – Spark DATA diagram for aluminum shaft in steel.

Peak sites observed represents spectral intensity obtained from the sparks that were struck nonmetallic inclusions containing aluminum. The base represents the distribution of metallic aluminum (soluble) uniformly distributed in the steel.

Processing of this pulse distributions with various mathematical algorithms allows to determine the soluble/insoluble part of an element, the number of inclusions, their size, and the linking of 2 or 3 or more channels we can identify complex types of inclusions and their characteristics.

2. EQUIPMENT USED

Determinations were made on an optical emission spectrometer ARL 4460 with 36 measurement channels of which 32 are equipped with Spark DATA technique.

May analyze of 27 chemical elements in iron base including residual elements: N, Zn, Zr, Cd, Pb, Hg, Mg. Source shaft is digital type CCS and works at 400 Hz.

In integration is used the TRS (time resolved spectrometry) method, each element having her own window of integration during the shaft. For the determination of Al and Ca, our elements of interest in the study, are used channels: for Al the channel with number 7 (with wavelength 394.22nm), the calibration field between 0.0003% up to 0.093%, a standard deviation SEE = 0.00248 and the correlation coefficient R=0.991; for Ca the channel with number 3 (with wavelength 396.85nm), calibration field between 0.00007% up to 0.0043%, a standard deviation SEE=0.00010 and the correlation coefficient R = 0.994.

3. DETERMINATION OF INSOLUBLE PART IN Al AND Ca

Determination of insoluble part goes to flash diagram obtained by Spark DATA technique. Determination of soluble/insoluble parts is through statistical processing of the charts. Mathematical algorithm Ca_tot calculates the average value associated with total calcium in the sample, the algorithm Ca_sol calculates the median, associated with soluble calcium, Ca_ins algorithm calculates the difference between average and median associated with insoluble calcium. Knowing the total calcium in the sample from the calibration curve is determined:

$$\text{Ca ins} = \text{Ca} * \text{Ca\_ins}/\text{Ca\_tot}.$$

In the same way is calculated the insoluble aluminum. Having the Spark DATA diagram as a base we can calculate the soluble/insoluble part at other Items of interest in steel, as B, Ti, Mg.

Verification of the method was done on a set of reference materials CKD 180–189 with certified values of soluble Al. In Table 3 are presented the comparative dates between measured values and certified values. Note that the measured values are found in the uncertainty limits of certified values, so the Spark DATA technique offers with the soluble/insoluble applications, results with good accuracy.

The advantage of this technique of measurement is that it offers the possibility to determine the soluble/insoluble part of an item without the need for calibration curves, respectively of the reference materials that have certified fraction soluble/insoluble.

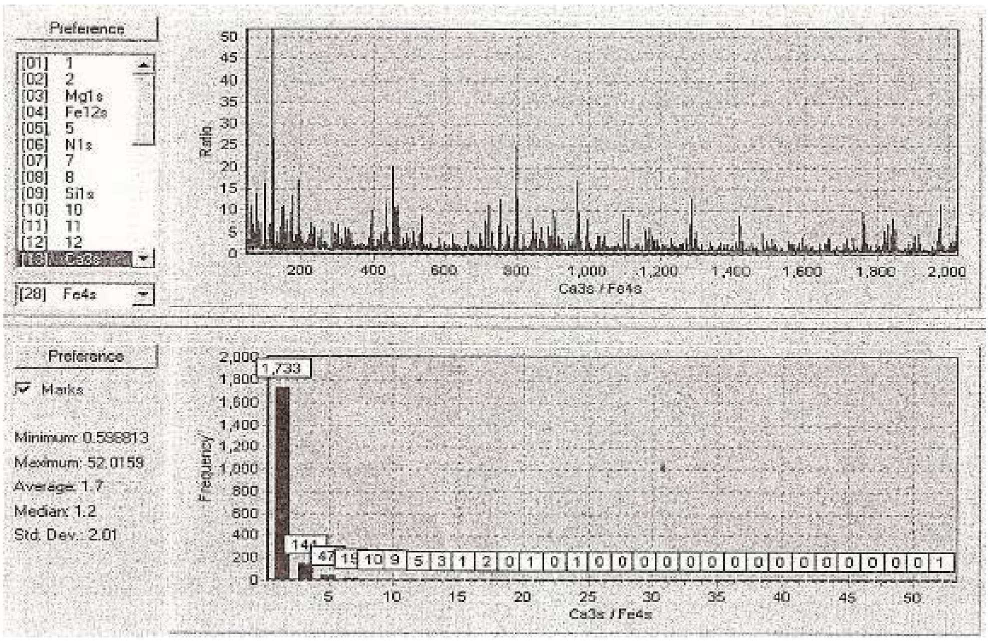

Fig. 2 – The Spark DATA diagram on Ca channel, obtained in 2000 sparks, for a sample of steel with Ca_{tot} = 0.00200 %; Ca_{ins} = 0.00056 %.

Table 1

The comparative table between values certified by soluble aluminum and those measured by the Spark DATA technique

Reference Material	Certified values (%)			Spark DATA (%)		
	Al Tot	Al Sol	Tot/Sol	Al Tot	Al Sol	Tot/Sol
CKD 181	0.016±0.001	0.014±0.001	1.00 - 1.31	0.0147	0.0141	1.04
CKD 182	0.023±0.001	0.017±0.002	1.16 - 1.60	0.022	0.019	1.16
CKD 183	0.150±0.005	0.141±0.006	0.99 - 1.15	0.151	0.146	1.03
CKD 184	0.022±0.002	0.016±0.002	1.11 - 1.71	0.023	0.017	1.35
CKD 185	0.060±0.002	0.054±0.004	1.00 - 1.24	0.0595	0.0565	1.05
CKD 186	0.042±0.002	0.038±0.003	0.99 - 1.24	0.043	0.041	1.05
CKD 187	0.019±0.002	0.017±0.002	0.90 - 1.40	0.021	0.019	1.10
CKD 188	0.093±0.003	0.083±0.004	0.90 - 1.40	0.095	0.086	1.10
CKD 189	0.041±0.003	0.039±0.003	0.93 - 1.19	0.042	0.040	1.05

4. INCLUSION ANALYSIS

We'll show how the Spark DATA technique can determine the nonmetallic inclusion in steel, type, content, size and distribution of inclusion in the sample.

The Spark DATA diagram allows the combination of 2, 3 or 4 channels measure. We saw that a peak in the diagram is an inclusion for the specified element. Once you get peaks on two channels at the same spark, means that we have a nonmetallic inclusion which contains those two chemical elements.

Similarly we can determine if the specified inclusion contains 2, 3 or 4 chemical elements in their composition and their proportion. In Fig. 3 is shown the Spark DATA diagram for aluminum and calcium channels for a sample of steel.

From this diagram can be determined the number of inclusions Al-Ca type, their size and the quantitative proportion of the two elements in an inclusion. By using the algorithm Sdat Count can be obtained the total number of inclusions by type Al-Ca as the peaks with intensity the 3 times standard deviation of the fund or the number of large inclusions as the number of the peaks with intensity over 6 times standard deviation.

A large inclusion is a greater intensity on channel, intensity that is proportional to the concentration element in the specified inclusion. Based on the ratio of spectral intensities of the two elements and the relative sensitivities of the two channels measure we can determine the concentrations report of the two elements in the inclusion.

As well we can study the inclusion of S-Ca type of diagram shown in Fig. 3.

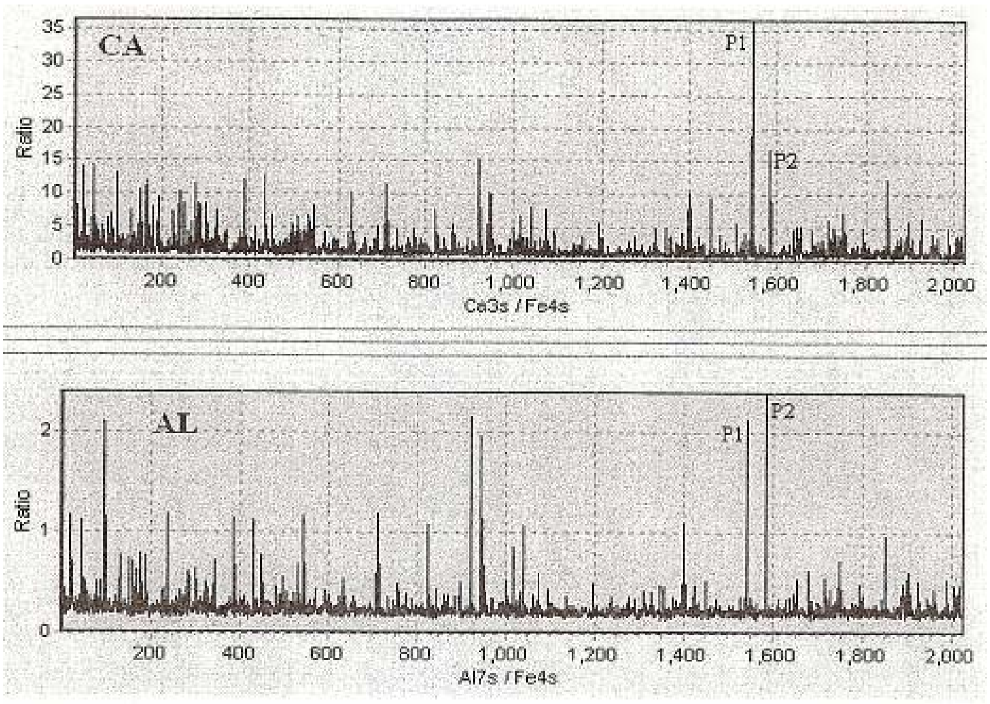

Fig. 3 – The Spark DATA diagram for Al and Ca channels on the final sample from S1.

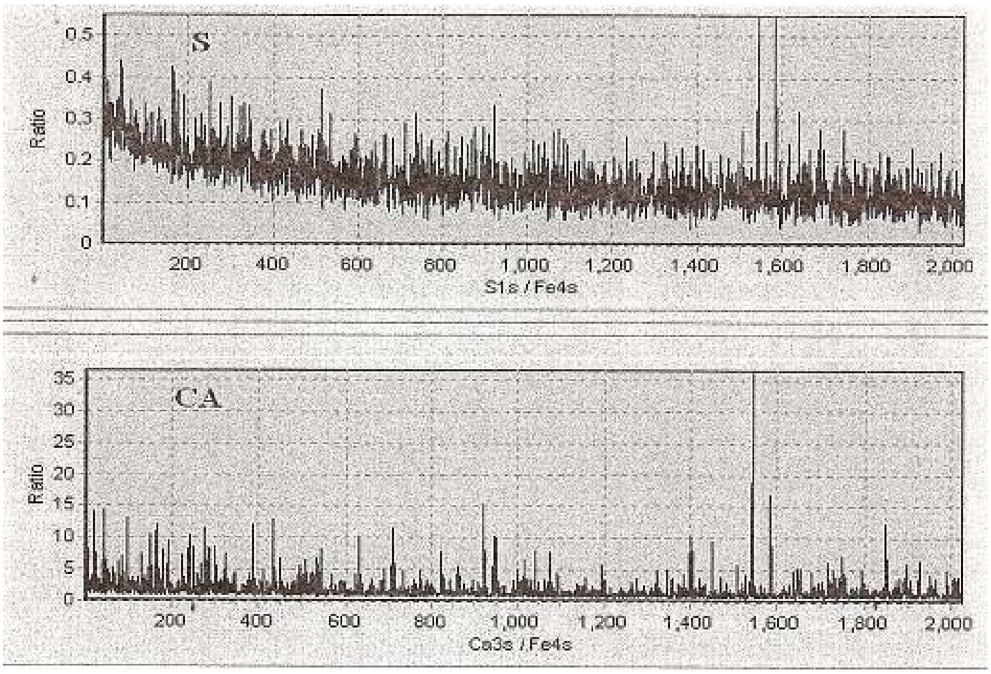

Fig. 4 – The Spark DATA diagram for S and Ca channels on the final sample from S1.

5. EXPERIMENTAL DETERMINATIONS

Measurements were performed using optical emission with spectrochemical method – Spark DATA technique on three samples S1, S2, S3. Results of determination of the insoluble fraction and As for the 3 samples are presented in Table 2.

Table 2

Results obtained in the determination of Al insoluble and Ca insoluble in three samples of steel C40 mark, is continuously cast

Samples	Al tot (ppm)	Al ins (ppm)	Al ins (ins/tot)	Ca tot (ppm)	Ca ins (ppm)	Ca (ins/tot)	$\frac{Ca_{tot}}{Al_{tot}}$	$\frac{Ca_{ins}}{Al_{ins}}$	$\frac{CaO}{Al_2O_3}$
S1	85	4	0.047	25	8	0.320	0.29	02	1.49
S2	150	6	0.050	33	9	0.273	0.28	1.5	1.12
S3	80	16	0.20	5	2	0.333	0.07	0.13	0.09

Technological requirements impose the following conditions in calcium treatment of cast steel, with influences on the behavior of the casting of liquid steel and the structure and quality of cast product.

A first condition is that the ratio Al ins/tot to be below the limit established by the technology. We observe sample S3 has different ratio Al ins/Al tot of the other two samples S1 and S2, is approximately an order of size greater than the other two. This creates conditions of inappropriate behavior at the continuous casting.

A second condition is that the ratio *x* to be above the established technology. We observe sample S3 has different ratio Al ins/Al tot of the other two samples S1 and S2, is approximately an order of size greater than the other two. Samples S1 and S2 accomplish this condition, but the sample S3 is well below the other two samples.

A third condition is related to calcium content. It should not be any small case that favors the formation of aluminum compounds with melting temperatures above 1700^{o}C and which remain solid at the temperature of a steel casting. Nothing too great, in case that favors the formation of calcium sulphide with melting point above 2400^{o}C.

Aluminum compounds which need to be avoided are any form of CaO* 6 Al_2O_3 (CA6) with melting temperature of 1833^{o}C, CaO * 2Al_2O_3 and (CA2), which has melting temperature of 1775^{o}C. Aluminum compound form CaO* Al_2O_3 (CA) with the melting temperature of 1590°C is the temperature limit of steel casting. Alumina is the first report CaO/Al_2O_3 of 0.09, with high temperatures melting in alumina calcium that is liquid at the temperature of the casting of steel, meaning the one with melting temperatures below 1550^{o}C.

The first compound of aluminum has the ratio CaO/Al_2O_3 of 0.09, 0.028 for second and third by 0.54. The goal of treatment with calcium is to transform alumina, with high melting temperatures, in compounds of aluminum and calcium which are liquid at the temperature of a steel casting that is the melting temperatures below 1550^{o}C.

The perfect aluminum compounds would be: 3CaO* Al_2O_3 (3CA) or 12CaO* 7Al_2O_3 (C12A7) with melting temperatures of 1539°C 1395°C respectively with the CaO/Al_2O_3 of 1.63 respectively 0.92. A good treatment involves calcium content of calcium in liquid steel over 25 ppm, so that calcium content in alumina are more than 25% calcium oxide, or over 35%. This means that the CaO/Al_2O_3 to be over 0.54.

Initially, it is believed that all insoluble aluminum and calcium are found in the form of alumina, the ratio of Ca ins/Al ins, can cause a medium CaO/Al_2O_3 in aluminum compound trained. Analysis of data from Table 2 show that sample S1 has calcium content and the limits mentioned under CaO/Al_2O_3, and therefore have formed solid alumina at the temperature of a steel casting. Regarding the types of inclusions formed by Spark DATA analysis of 3 samples were obtained the data in Table 3.

Table 3

Inclusional analysis with Spark Data on S1, S2, S3 samples

Samples	The types, sizes and numbers of nonmetallic inclusions										
	Al	Al big	Al & Ca	Al & Ca big	Al & Ti	Al & Si	Al & N	Al & Ca &Si	Ca	Ca big	Ca & S	Ca & S big
S1	51	9	43	4	1	0	0	0	87	7	12	2
S2	60	5	51	3	1	0	0	0	103	4	15	1
S3	49	11	27	6	0	0	0	0	45	3	3	0

From the data presented is seen that the largest share of measuring nonmetallic-inclusion are those which are aluminum and calcium composition. Observing the correlation with the other elements analyzed, we can say that these inclusions are the type Al-CaO, so alumina calcium. A relatively small number of inclusions containing only Al respectively Al_2O_3, or Ca, respectively CaO, a normal result in the steel treated with calcium. It's observed the presence of Ca-S inclusions, respectively CaS. Inclusions considered small, with peak height of between 3-6 times the standard deviation of the fund, did not share important in analyzing purity. Important inclusion is the one large with peak's height over 6 standard deviations. We analyze several large alumina inclusions from the 3 samples to determine their concentration and type of alumina formed. Peak in Fig. 3 sites P1 and P2 represent two alumina in order of size of sample S1. Peak in Fig. 5 sites P3, P4, P5 is the first order in 3 alumina size of sample S3.

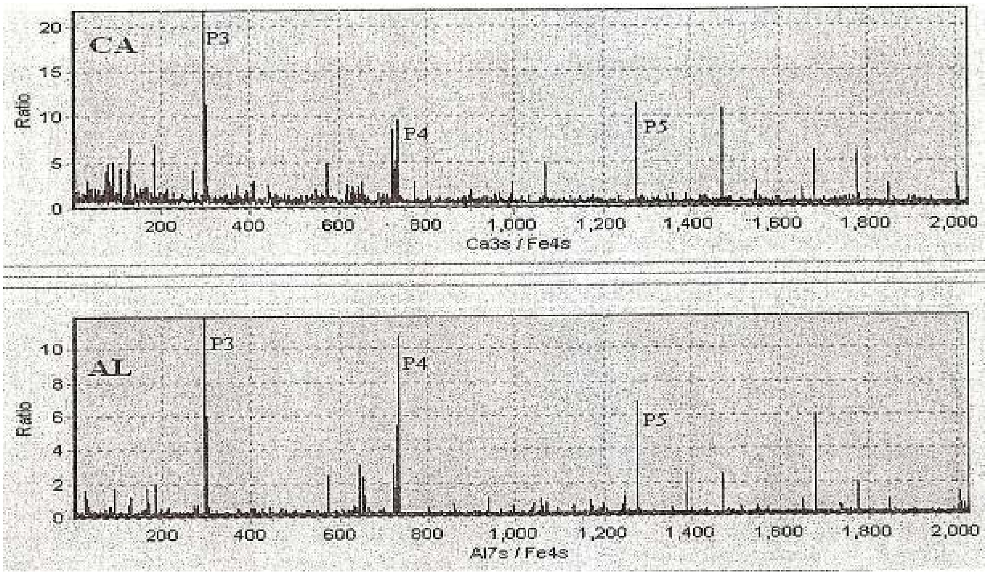

Fig. 5 – The Spark Data for the channels of aluminum and calcium in the sample S3.

Of peak intensities of the two sites and taking into account the sensitivity *S* of the Ca channel is an order size greater than that of aluminum, we can determine the concentrations of *R* between Al_2O_3 and CaO in alumina and so the alumina type format. Results are presented in Table 4.

Note that if aluminum compounds P1 and P2 of the sample S1 are the "good" type of C3A, C12A7 and CA with melting points below 1550°C, the aluminum compounds P3, P4, P5 of sample S3 are the "bad" type and CA6 CA2 with melting points above 1750°C.

Tabel 4

Identifying the type of alumina in the samples S1 and S3

Peak	Number of spark	$(I_{Ca}/I_{Fe})/S(I_{Al}/I_{Fe})$	*R* measuring (%CaO)/(% Al_2O_3)	*R* type of alumina	Identification
P1	1543	1.72	1.27	*R*(3CA) = 1.63 *R*(C12A7) = 0.92	Alumina mixture C3A şi C12A7
P2	1584	0.71	0.53	*R*(CA) = 0.54	Alumina CA
P3	296	0.18	0.14	*R*(CA6) = 0.09 *R*(CA2) = 0.28	Alumina mixture CA6 şi CA2
P4	732	0.09	0.07	*R*(CA6) = 0.09	Alumina CA6
P5	1275	0.16	0.11	*R*(CA6) = 0.09	Alumina CA6

Identifying these types of alumina in the sample S3 correlated with data from Table 2 that the average CaO/Al2O3 shows us that the presence of the aluminum compounds type CA6, respectively CA2, are solid at the temperature casting of steel

6. CONCLUSIONS

From the data presented we establish that the spectrochemical method of optical emission, technique Spark DATA, is a useful method of treatment with calcium in continuous casting of steels. This method can measure the main parameters of control for a good treatment with calcium, respectively aluminum contents and calcium at level ppm, insoluble fraction of these elements, type, size and number of inclusions formed, and respectively the types of compounds aluminum formed. This has the advantage that can be provided in real time during the making process, allowing the entire corrective action process. Method OES - Spark DATA has a great potential for development in the analysis of steels, allowing determinations of soluble-insoluble type at any item of interest in steel, inclusional analysis, respectively the determination of number, type and size as well as nonmetallic inclusion determinations default content from oxygen as a measure of purity steel.

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