

Determination of TiB₂ inclusions in Al-billets by single spark emission spectrometry

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DETERMINATION OF TiB₂ INCLUSIONS IN AL-BILLETS BY SINGLE SPARK EMISSION SPECTROMETRY

Marcel Rosefort, Hubert Koch, Frank Urbanek
TRIMET ALUMINIUM AG, Aluminiumallee 1,
45356 Essen, Germany

Joerg Niederstrasser
OBLF Gesellschaft für Elektronik- und
Feinwerktechnik mbH, Salinger Feld 44,
58454 Witten, Germany

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Abstract

Aluminum safety parts and aluminum bright shining components, especially for automotive applications, have to be nearly free from inclusions due to their influences on mechanical properties and surface quality, respectively. On the other hand grain refinement is essential. For this purpose titanium/boron based master alloys are often used, which can lead to TiB₂ agglomerations in the billet. The usual method for quality control is microscopy of the specimen.

The growing demand for high quality billets has created a need for faster and cost-efficient methods of quality control. Single spark spectrometry promises fast determination of inclusions, especially of TiB₂-particles. Statistical evaluation of single spark spectrometry data allows the determination of distribution and size of TiB₂-agglomerations.

This paper covers the application of single spark emission spectrometry to Al-billets, the graphical and statistical analysis and an outlook on the quality control using single spark emission spectrometry.

Introduction

The need for new advances in all fields of materials technology, in particular the automotive industry, increases the requirements on aluminum billets produced by continuous casting. Al-billets are often converted to automotive components like safety parts and bright shining components. Regarding the high quality requirements, e.g. mechanical properties or surface quality of bright shining parts, Al-billets have to be nearly free from inclusions.

The determination of the inclusion content in Al-billets is currently made by time-consuming microscopy of speci-

mens. New methods are in demand for higher efficiency. A timesaving method would be the spark emission spectrometry, which is usually used for the analysis of aluminum alloys. Gated Integration of Single Sparks (GISS) potentially enables the combination of alloy analysis with the determination of inclusions in aluminum alloys. The TRIMET ALUMINIUM AG and the OBLF GmbH cooperate for the investigation of this method.

The TRIMET-Group provides the aluminum processing industry with primary metal, alloys, semi-finished products, castings and recycling. The competence of the business unit PRIMARY PRODUCTS is continuous casting in a wide range of formats and properties, high quality material for the automotive industry and their suppliers. Products are rolling slabs, extrusion and forging billets, hot dip-coating alloys, initial products for safety parts and liquid aluminum. The demand for high quality and services regarding these products is essential to enforce and secure the quality control.

OBLF GmbH is one of the world's most important developers and manufacturers of stationary spark emission spectrometers for the analysis of metals and alloys. Typical customers are primary producers or other smelters, metal processing companies, research institutes and universities. The spectrometers can be used manually or they can be integrated in fully automated laboratories.

Optical emission spectrometry

The standard analysis method in a process laboratory of the aluminum industry to determine the chemical composition of aluminum and aluminum alloys is the spark emission spectrometry. It is a technique, which involves placing the sample on a spark stand and exposing it to electrical spark discharges with frequencies of up to one kHz in an argon atmosphere. The vaporized sample material is split into atoms or ions in the hot spark plasma. Following thermal excitation, these atoms or ions emit light of characteristic wavelengths. This light is fed into the optical system via an entrance window, is then spectrally separated with the help of an optical grid and is finally detected by photomultipliers. The quantity of light is a measure of the mass content of the respective element in the sample; the measured value can be converted into a mass content by means of calibration.

The sparking process is split into three main phases: a purging, a pre-sparking and an integration time. During the purging phase, the spark stand is purged of air with argon for some seconds. The pre-sparking phase involves homogenizing a part of the sample surface in order to

minimize the influence of the sample structure or inclusions on the average analysis result. The inclusions should be destroyed or remelted during this period. The integration phase follows after this, during which the light emitted in the course of several thousand discharges is measured and integrated. The result is one intensity value per element, which corresponds to the content of the element in the sample. It is a statistical value over the analyzed surface. In standard spectrometers no information about the single discharges is available.

Single spark spectrometry and GISS

Thanks to cutting-edge data-logging technology and rapid data processing, it is now possible to log the intensities of all individual sparks of a measuring channel. In comparison to a standard spectrometer without the single spark technique, the average of all individual intensities is converted into the average mass content value.

Additionally, all information about the local chemical composition at the points of impact of the individual sparks therefore remains intact. The advantage is that inhomogeneities in the sample surface (e. g. inclusions) can be detected. Clear differences are visible if one observes a metal sample with a few and one with a greater proportion of non-metallic inclusions as well as the corresponding individual spark diagrams (the first 1000 single sparks) of one element, which is solved in the base and segregated in inclusions, Figure 1.

Nearly all the intensities of the clean sample are within a narrow field. In contrast, the sample with inclusions displays many very high intensities. These represent sparks that have hit inclusion particles or the grain boundaries between the base metal and the inclusion. These high intensities can be statistically evaluated and correlated with metallurgical information about the quality and quantity of inclusions or the purity grade.

This technique is generally called single spark spectrometry or PDA (Pulse Discrimination Analysis).

It provides a number of advantages:

- detection of bad samples due to blow holes or inhomogeneous samples (critical when operating automated systems)
- differentiation between metallic and non-metallic shares (phase analysis, for instance: aluminum "soluble / insoluble" in steel)
- detection of inclusions

Over the last years this method has become more and more popular, especially in the steel industry to detect inclusions such as aluminum oxide [1].

In addition to the single spark spectrometry, the OBLF spectrometer also makes it possible to freely define the starting point of the integration periods of individual sparks for each measuring channel, as a result of which the emitted light will only be detected in certain, discrete time windows. The main aim of this "time-resolved spectroscopy (TRS)" is to improve the signal-to-noise ratio such as to guarantee the lowest possible detection limits for each element by intelligently screening-out signal bandwidths that display a high degree of background radiation.

At OBLF, the combining technique of TRS and single spark spectrometry is called GISS (Gated Integration of Single Sparks).

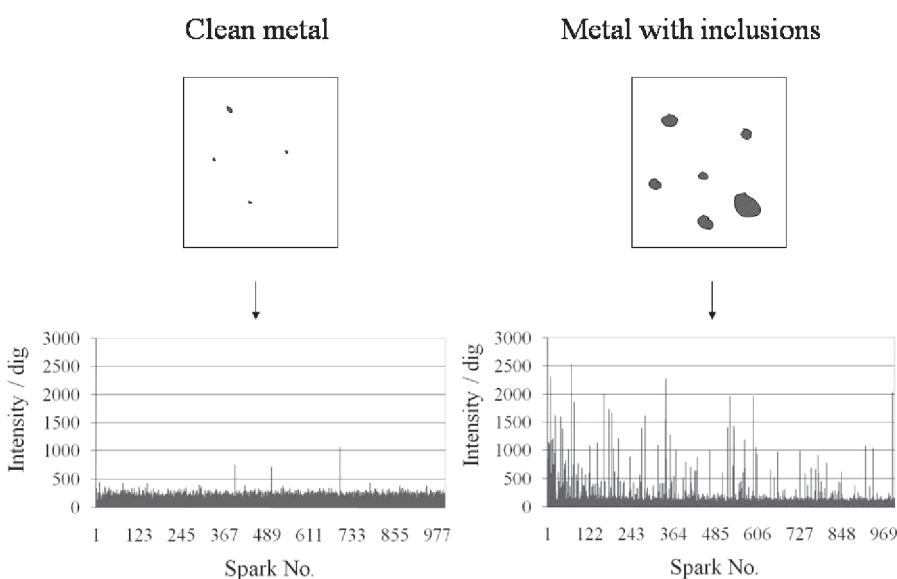


Figure 1. Differences between a metal sample with a few and one with a greater proportion of non-metallic inclusions and the corresponding individual spark diagrams (first 1000 single sparks) of the element, which is solved in the base and segregated in inclusions.

Inclusion Detection

TRIMET processes more than 450 different alloys and additional special alloys according to customer specification for approximately 100 different billets diameters. All these billets especially the billets for aluminum safety parts and aluminum bright shining components have to be nearly free from inclusions. In this investigation the examined materials are EN AW-6060 [AlMgSi], EN AW-6082 [AlSi1MgMn], EN AW-6061 [AlMg1SiCu], Al99.9MgSi and EN AW-6951 [AlMgSi0,3Cu] as a choice of alloys.

Often found and typical inclusions in aluminum billets are TiB₂-agglomerations caused by grain refinement. The detection of inclusions by GISS is exemplarily investigated with TiB₂-inclusions. Further inclusion types will be investigated in the future.

The dimensions of the investigated TiB₂-agglomerations are between 10 up to 700 μm diameter, Figure 2 a) to c). Especially the larger TiB₂ agglomerations are often found in combination with aluminum oxides, Figure 2 c). Specimens without inclusions are analyzed for comparison. This should enable to differentiate between specimens with inclusions and faultless billets.

In this project the first step of each examination of a specimen was the determination of the inclusions concerning dimensions and composition by microscopy, Figure 2 a) to c). After a detailed analysis of the inclusion an examination with a spectrometer with gated integration of single sparks followed.

The system used is the spectrometer OBLF QSG 750 with GISS technology. The main features are:

- simultaneous spark emission spectrometer,
- Paschen-Runge line-up,
- 750 mm Rowlang circle,
- 54 analytical channels,
- temperature stabilized,
- Gated Digital Source,
- single spark intensities available for all analytical channels.

For the detection of inclusions in Al-billets the analysis of single spark intensities is essential. Referring to this an advantage of the used spectrometer is the easy possibility of spark intensity adjustment.

Low single spark energy is conducive to the detection of inclusions [2]. The lower energy leads to a slighter melting of the specimen. So there is less homogenizing of the inclusions and more and better defined single spark intensities for the inclusion elements, Figure 3 a) and b). Additionally, the average and the standard deviation are lower. So the outliers caused by the TiB₂-inclusion are readily identifiable, Figure 3 a).

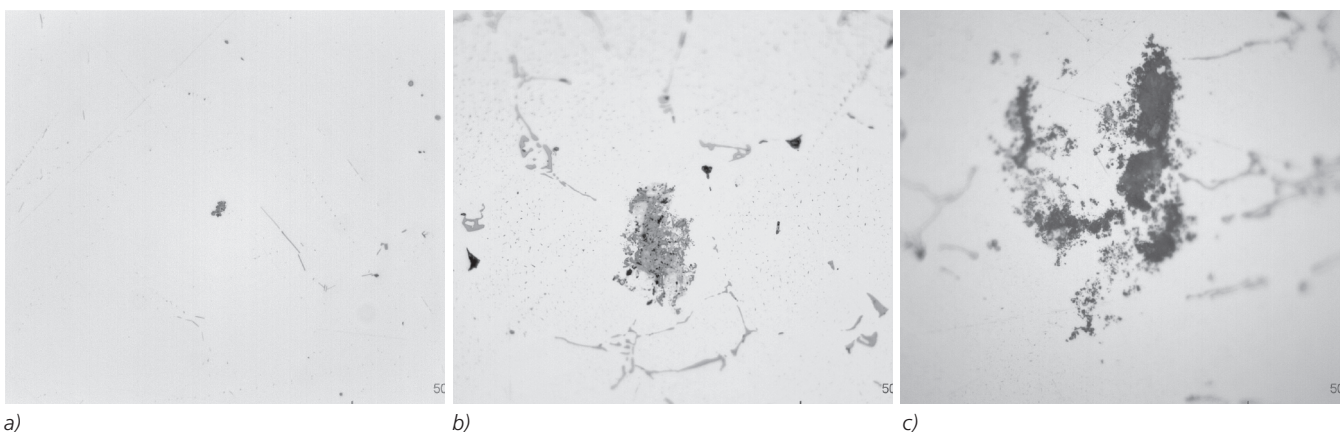


Figure 2.

a) Al99.9MgSi alloy with a 10 μm TiB₂ agglomeration.

b) EN AW-6082 [AlSi1MgMn] alloy with a 50 μm TiB₂ agglomeration.

c) EN AW-6082 [AlSi1MgMn] alloy with a 110 μm TiB₂/Oxide agglomeration.

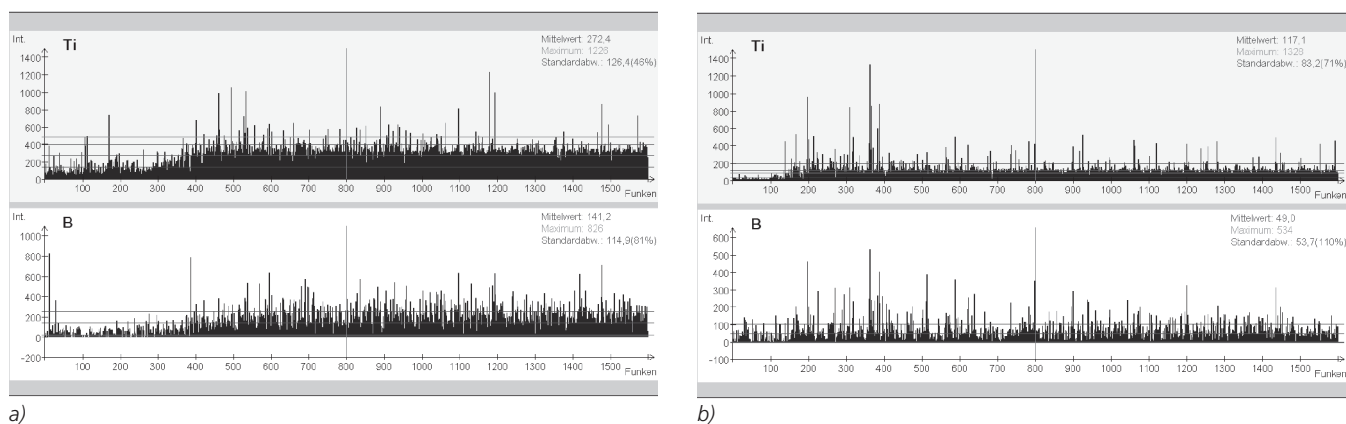


Figure 3.

- a) Single spark diagram for Ti and B of the specimen 116-1893 with high spark energy. Ti: Average: 272.4; Maximum: 1226; Standard deviation 126.4, 46%; B: Average: 141.2; Maximum: 826; Standard deviation 114.9, 81%
- b) Single spark diagram for Ti and B of the specimen 116-1893 with lower spark energy. It can be clearly seen that the average and the standard deviation are lower and outliers caused by the TiB₂-inclusion are readily identifiable.

The GISS data are statistically evaluated, especially the single spark intensities that are above average for both titanium and boron and can thus be identified as an inclusion caused by these two elements. Such spark intensities will be named below as “inclusion markers”. Exemplarily the main analyzed statistic parameter both for titanium intensities and for boron intensities are listed:

- average,
- standard deviation,
- number of spark intensities above standard deviation,
- maximum,
- percental value of maximum related to average,
- sum of spark intensities above standard deviation,
- skewness.

Statistical Analysis of the Sparking Process

The main target of this project is to determine inclusions and their dimensions in Al-billets. The principle is to detect inclusions in bad samples simply by evaluating the corresponding channel. If there is a TiB₂-inclusion some sparks will hit the inclusion and the Ti- and B-channels should display clearly higher intensities, Figure 1.

However the statistic analysis shows that mostly it is not possible to differentiate so easily between clean samples and samples with inclusions. There is a clear statistical spread. Mainly with higher spark intensities the statistical spread is significant. Though there is evidence that the titanium and boron intensity values and distributions

are related to the inclusion dimensions, the great spread prevents a prediction of inclusion and inclusion size by analyzing univariate correlations. As an example Figure 4 shows the skewness of the boron intensity histogram.

Shorter discharge times, i.e. lower spark intensity, enhance the results. Accordingly the correlations between single statistic values and the dimensions of the inclusion pictured in Figure 4 to Figure 7 become more apparent. A couple of statistic parameters, e.g. the sum of all spark intensities for the inclusion markers or the standard deviation of the single spark intensities, gives analyzable results. For example the sum of all inclusion marker intensities, Figure 5, has a good correlation with the inclusion dimension. The correlation can be seen more clearly in logarithmic chart in Figure 6. The diagram for the standard deviation of the intensities looks similar, Figure 7. These kinds of parameters relations give first hints on the inclusion dimensions in Al-billets.

Because the fit R² is not very good for these univariate relations (values around 0,5 to 0,65), the next step is a bivariate and multivariate analysis of the different parameters. As exemplification the bivariate correlations of the inclusion dimension with the maximal intensity values and the skewness of the intensity histograms are listed below, Figure 8 and Figure 9. A more clear relation between cleanness of the aluminum and the sparking parameters can be seen.

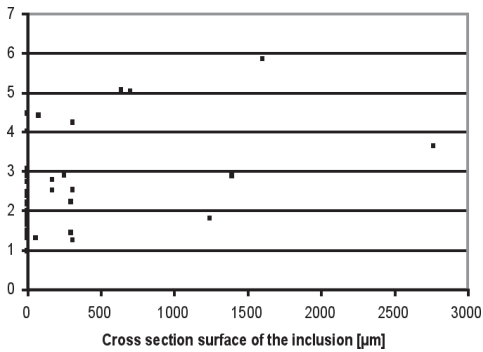


Figure 4. A trend is visible for the relation between skewness of the boron intensity histogram and the inclusion dimension. But the statistical spread is significant.

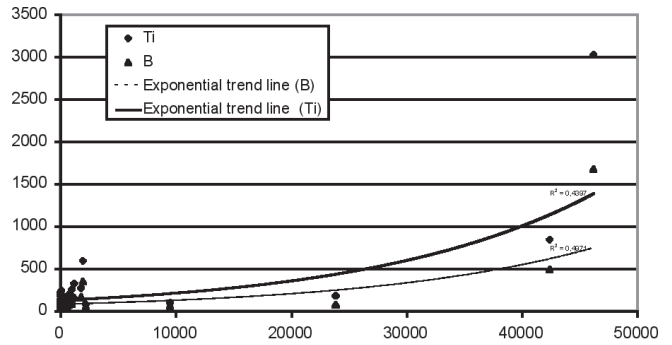


Figure 7. Standard deviation of the spark intensities of Ti and B in relation to the inclusion dimension.

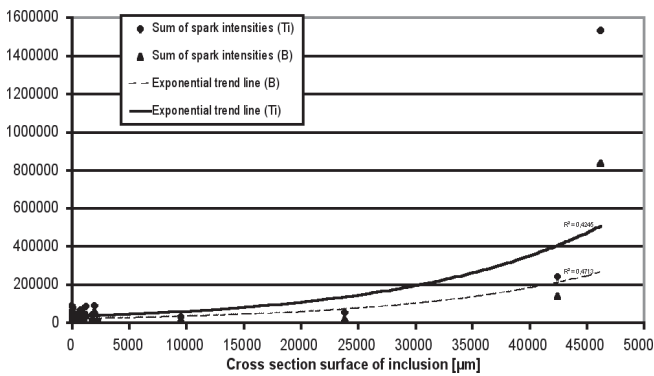


Figure 5. Sum of the spark intensities only for the inclusion markers.

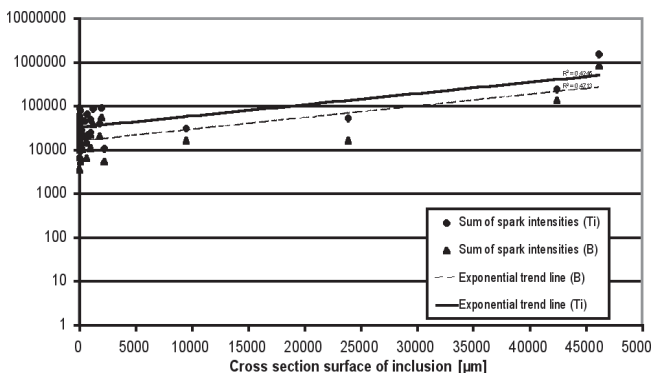


Figure 6. Sum of the spark intensities only for the inclusion markers with a logarithmic Y-axis.

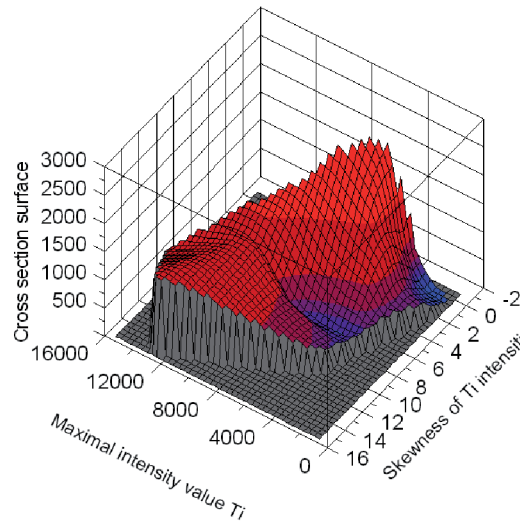


Figure 8. Bivariate correlation of the inclusion dimension with the maximal intensity value (Ti) and the skewness of the Ti intensity histograms.

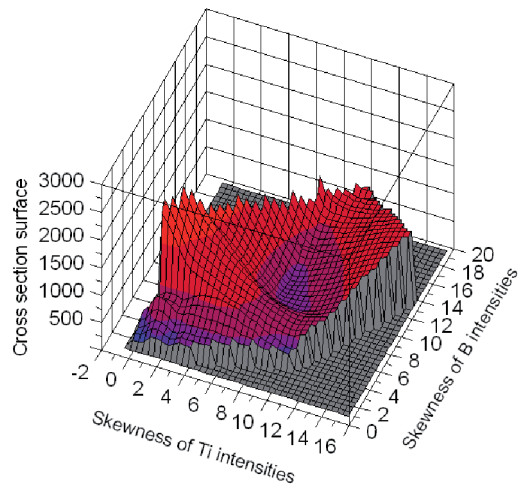


Figure 9. Bivariate correlation of the skewnesses of the Ti and B intensity histograms.

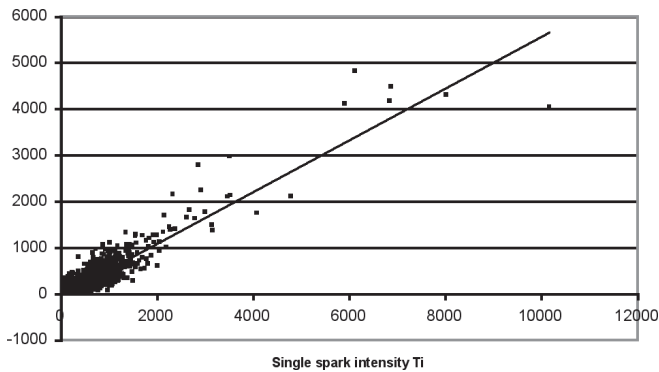


Figure 10. Correlation diagram of a spark analysis for an aluminum billet (Si1, Specimen 109-3133) with a TiB₂-inclusion (cross section surface: 1246 μm²).

Another approach is the analysis of the element ratio. Should both elements, Ti and B, responsible for an inclusion, exist in the spectrometer channels used for the analysis, single spark diagrams can be viewed for both together, as shown in Figure 3. The single spark intensities that are above-average for both titanium and boron can be identified as an inclusion caused by these two elements. This is made particularly clear by the correlation diagram in Figure 10. A TiB₂-inclusion yields a theoretical proportion of the elements Ti and B. Expressed as the proportion of spark intensities it is:

$$\frac{\text{Ti}}{\text{B}} = 0,47$$

In reality it can be observed that all specimens with TiB₂-inclusions have at least a Ti/B value of 0,47. But many samples have a clearly higher value up to 0,65. For example the specimen pictured in Figure 10 has a Ti/B value of 0,56 with a high fit R² of 0,78. Corresponding all these specimens have a low spread of the Ti/B values and to that effect a high statistic fit in the correlation diagram. On the other hand all clean samples show Ti/B value lower than 0,43. This correlation is diagrammed in Figure 11.

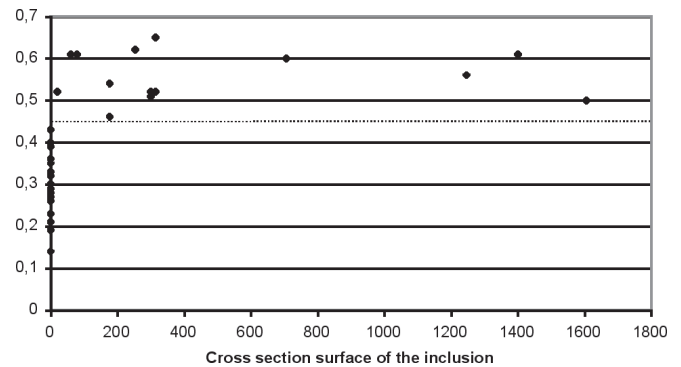


Figure 11. Correlation between inclusion dimension and the Ti/B values. All specimens without inclusions have value lower than 0,43. This limitation seems to be an applicable criterion for the identification of TiB₂-inclusions.

Conclusions

After the first tests it can be resumed that there are good prospects to develop a new method for TiB₂-inclusion determination in aluminum billets. The correlation diagram provides the possibility of inclusion detection and the statistical parameter analysis yields first coherences of the single spark diagrams with the inclusion dimensions.

This above-mentioned examination has to be continued. Furthermore a multivariate linear or non-linear regression is promising to increase the reliability of the inclusion prediction. The intention must be to reach the same or a better reliability of inclusion detection compared to microscopy.

Furthermore the same examination has to be carried out for the other relevant inclusion types in aluminum billets. If these aims are achieved it is reasonable to develop a spectrometer for automatic scanning of billets specimens with several sparking points. The addition of all these process and analysis advances can lead to a new and economical process for the determination of inclusions in aluminum billets.

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TRIMET ALUMINIUM AG • Aluminiumallee 1 • 45356 Essen
Telefon 0201-3660 • www.trimet.de