Application Note 41248

Ultra-fast analysis of micro inclusions in aluminum and its alloys with Thermo Scientific ARL iSpark Metal Analyzers – Standard Inclusion Analysis

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Key Words

ARL iSpark, Micro inclusions in aluminum, Process control, Qualitative size distribution, Clean aluminum, Inclusion analysis, Aluminum and its alloys

Goal

Perform ultra-fast analysis of micro inclusions in aluminum and its alloys

Introduction

Optical emission spectrometry (OES) is a fast, easy-to-use and cost-effective analytical technique used for elemental analysis of solid aluminum samples in various contexts, from production to recycling and from foundries to service laboratories. The Thermo Scientific™ ARL iSpark™ Series metals analyzer is a high-performance OES spectrometer platform delivering the ultimate precision and accuracy for the analysis of aluminum from trace to alloying element levels.

The Spark-DAT (Spark Data Acquisition and Treatment) methods considerably extend its capability beyond the spectrochemical analysis by also enabling ultra-fast inclusion analysis. In the steel industry, these methods are routinely used in order to gain information about the inclusions during the steel elaboration process. Recent developments and improvements increase its attractiveness for the aluminum industry, where inclusions also constitute considerable challenges. In aluminum and its alloys, inclusions affect for example fluidity, gas porosity, machinability, surface appearance and mechanical properties, and analysis of inclusions in the liquid aluminum is important. Spark-DAT analysis, available with the ARL iSpark, offers interesting potentials, in particular for replacing or simplifying the traditional techniques of inclusion assessment.

Benefits

The benefits of using the ARL iSpark 8860 or 8880 spectrometers with Spark-DAT methods are the following:

- Drastic reduction of investment costs for inclusion analysis. The spectrometer is capable of performing inclusion analysis in addition to analysis of elemental concentrations
- Information on inclusions is available shortly after sample taking. This offers unequalled perspectives for in-process control of the metal elaboration
- Extremely short time for inclusion analysis and related sample preparation. The sample and its preparation are the same as for standard OES analyses
- No additional cost and time for operations is required as compared to the standard OES spectrometer. Maintenance, service and sample preparation for inclusion analysis remain the same
- Inclusion analysis performed in parallel with the analysis of elemental concentrations possible for more than 30 samples per hour. Inclusion analysis can be performed on all samples analyzed by OES
- Detection of randomly distributed exogeneous inclusions is easier. It is possible to rapidly analyze very large surface areas.

Principles

With the Spark-DAT methods, different treatment principles are used compared to OES concentration analyses: instead of being integrated and translated into concentration, the light intensity values for all the single sparks are submitted to a special mathematical treatment.

The intensity of a single spark signal depends on the composition of the sample at the position struck by the corresponding single spark. If the concentration of an element in the ablated sample material is significantly higher than the concentration of its soluble form in the matrix, the outcome is an intensity peak. This is typically the case when a spark hits a sample area containing a Ti based inclusion (e.g. TiB_2), because the Ti concentration is much higher than in the metal matrix due to the contribution of the inclusion.

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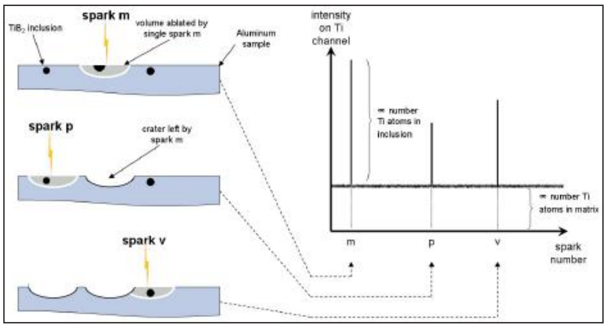
For a better understanding we can explain this with numbers: the concentration of Ti in a TiB_2 particle is ~69%, and if a spherical inclusion with a diameter of 5µm is ablated together with the sample material, this gives an apparent rise in the concentration of 0.136%. Graphically, this is illustrated by the following picture:



The intensity of the flat, noisy baseline signal is proportional to the concentration of Ti atoms dissolved in the matrix and the intensity of a peak depends on the amount of Ti atoms contained in the inclusion(s) ablated by a single spark. Consequently, the number of peaks is related to the number of such inclusions and their intensity to such factors as the inclusion size and the concentration of Ti in the inclusion.

Practical aspects

The Spark-DAT methods include software and specialized algorithms and are available with PMTs only. The single spark intensities acquired with SSA (Single Spark Acquisition) are used for inclusion analysis and traditional elemental concentration analysis, allowing the two types of analyses to be run simultaneously. Usually thousands of single intensity values are acquired on every channel, which makes the Spark-DAT raw dataset extremely large and complex. Because of this, fast dedicated algorithms are used to calculate the values corresponding to the information of interest.

The values calculated can then be handled like conventional OES results by the analytical software: they can be displayed, printed, stored, transmitted, used in pseudo-element calculations, checked against product specifications, etc.

Analysis time

The Spark-DAT analysis alone takes typically 7s for a single measurement (including 2s Ar flush). This mode is recommended only for quick counting and confirmation of inclusion types, and for obtaining raw data for off-line interpretation. However, the Spark-DAT analysis offers more possibilities when combined with the analysis in concentration. In this case, the analysis time taken between the start of the analysis and the display of the results is in average the following:

Application	Model	Time [s]
Pure aluminum	ARL iSpark 8860/8880	16
Low alloy Al and Al alloys	ARL iSpark 8860/8880	22

These analysis times (unchanged compared to standard elemental analysis) make inclusion analysis possible in many contexts, in particular during aluminum production, where analysis times are extremely critical.

Sample preparation

Milling which is the recommended surfacing technique for OES analysis of aluminum and its alloys guarantees a clean, unpolluted surface, ideal for inclusion analysis.

Contexts of use of Spark-DAT inclusion analysis

Spark-DAT inclusion analysis offers tremendous benefits for:

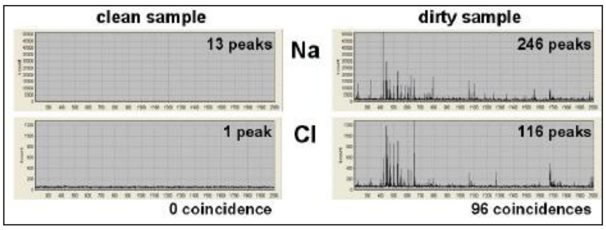
- Inclusion control for quality assurance. The most important application is inclusion analysis during aluminum and aluminum alloys production. However, interesting applications exist also for incoming materials or intermediate and finished products as well
- Process control via on-line monitoring of inclusions. The inclusions are “process markers or tracers” that indicate a change in the process. With Spark-DAT analysis they are monitored online, providing a unique way to take rapid corrective actions
- Sample screening. Hundreds of samples can be screened for inclusions in a day. This may help solving critical quality problems very rapidly. In a preventive approach, archived samples can be screened to verify if a quality problem signaled by a customer also affects products manufactured previously
- Replacement of long or costly analysis techniques. Spark-DAT methods can replace traditional techniques of inclusion analysis. It also offers the possibility to replace a technique that measures a property of aluminum or aluminum alloys which depends on the inclusions it contains (e.g. fatigue resistance), if correlation may be established between Spark-DAT inclusion analysis and the results of the said technique.

Evaluation of number and type of inclusions

The simplest application of the Spark-DAT methods consists in counting intensity peaks on the channel of a given element with the algorithm *Peaks*. A peak is defined as an intensity signal I_{peak} higher than a threshold situated at the mean intensity m of the element dissolved in the matrix plus three times its standard deviation SD:

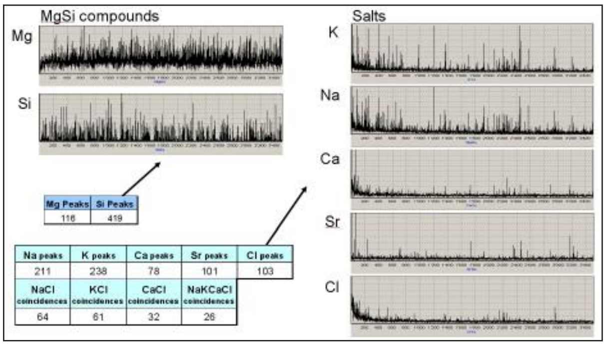
$$I_{peak} > m + 3 \cdot SD_{Imatrix}$$

Counting intensity peaks enables the evaluation of the number of inclusions containing this element. As shown in the following figure, clean and dirty aluminum samples can easily be identified by comparing the number of peaks counted on the channels of the inclusion elements.



The algorithm *Composition* allows counting coincidental peaks, i.e. peaks appearing on the channels of several elements concurrently during the same single spark. The coincidence of a peak on Na and Cl channels means that these two elements are part of the same inclusion, for instance a sodium chloride (NaCl) inclusion. In the previous example, no NaCl coincidence was counted in the clean sample and 96 were counted in the dirty one.

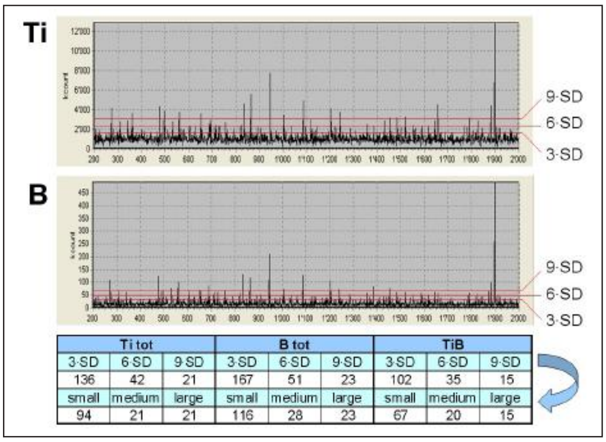
Coincidences of up to four channels can be counted with the algorithm *Composition*. This enables the chemical formulation of complex inclusions inter-metallic phases or inclusion clusters, as demonstrated with NaKCaCl in the following spark intensity diagrams of several elements recorded in an AlSi sample with 7% Si. Furthermore, the possibility to check for non-coincidences in addition to coincidences helps remove ambiguities on the inclusion type.



Note that other algorithms delivered with the optional Spark- DAT methods can be used in the Spark-DAT analysis of aluminum alloy samples, for instance Soluble. This algorithm evaluates the soluble fraction of an element and allows calculating the concentration of the soluble part of this element. Soluble is routinely used in steel samples analysis to evaluate the soluble part of Al, B, Ca and Ti.

Qualitative size and size distribution

Knowing the size of the inclusions or, better, their size distribution is important, since large inclusions are normally the most detrimental to the metal quality. The two algorithms *Peaks* and *Composition* can also be used in order to count signals belonging to different intensity classes. Because the peak intensity is related to the volume of the inclusion, these classes can qualitatively be considered as size classes. Setting the threshold 3•SD above the intensity of the element in the matrix allows the counting of all visible peaks. Setting it higher, for example at 6 or 19•SD as in the following example, allows counting only the inclusions of larger size, above 9 or 15•SD respectively.



Calculating the inclusions between consecutive threshold values provides the number of inclusions in the size class that they delimit. In the example, the number of peaks and coincidences between 3 and 6•SD correspond to small size inclusions, between 6 and 9•SD to medium size inclusions and higher than 9 to large size inclusions. Such calculations allow generating qualitative inclusion size distributions.

Inclusions detectable with Spark-DAT methods

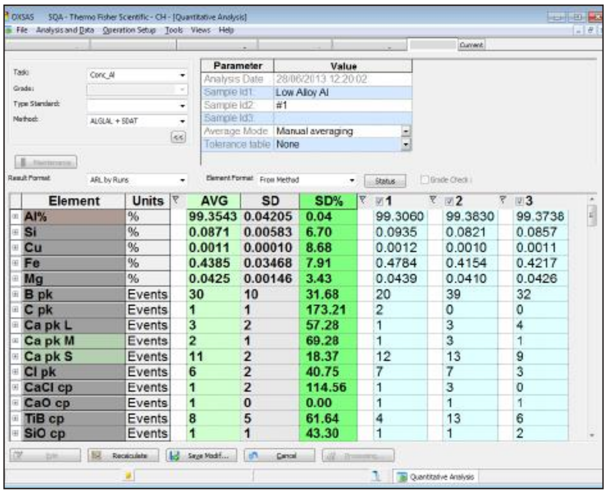
Various types of endogenous and exogenous inclusions may be observed directly or indirectly in aluminum and its alloys with the ARL iSpark spectrometer with optional Spark-DAT methods, e.g. oxides (Al_2O_3, MgO, CaO, FeO, MnO, SiO_2), spinels ($MgAl_2O_4$), carbides (TiC, Al_4C_3), borides (TiB_2), nitrides (AlN), salts ($MgCl_2$, NaCl, KCl, $CaCl_2$), graphite, intermetallic compounds (Cr-Mn-Fe), and various other compounds (AlP, Mg_3P_2, sulfides, AlB_2, Al_4C_4B).

The detection of an inclusion is limited mainly by the sensitivity of the analytical lines used, by the size of the inclusion and by the concentration level of the inclusion elements as soluble elements in the matrix: higher line sensitivity and lower soluble content allow determining smaller inclusions. For example in an aluminum sample with 100 ppm of Ti, the minimum detectable ESD is about 0.8 µm, while with 0.3% of Ti the minimum ESD detectable is 1.5 µm.

Low sensitivity of the oxygen line and Al being the matrix element explains the challenge to achieve direct observation of Al_2O_3 .

On-line analysis

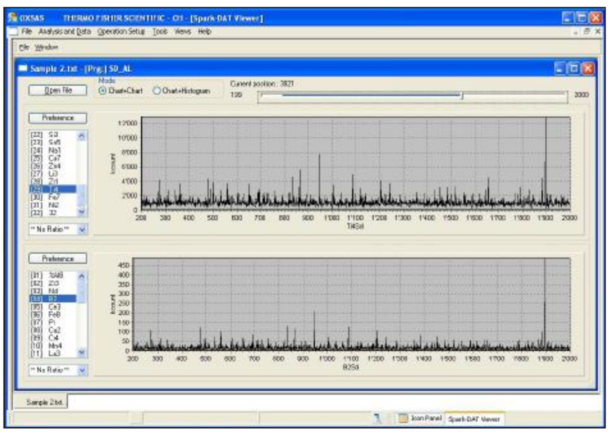
The results of Spark-DAT analyses, number of intensity peaks and number of coincidental peaks, can be monitored simultaneously with concentration values. The Spark-DAT results can be processed (for example used in order to calculate advanced parameters with so-called pseudo-elements), displayed, transmitted and stored like any standard OES result.



The above OXSAS screen shows partial results of an analysis including elemental determinations and inclusion related information (peak counts, qualitative size distribution – for inclusion size classes “Small”, “Medium” and “Large”, and counts of coincidental peaks).

Off-line investigations

The Spark-DAT intensity data can be stored in standard text (.txt) or comma separated value (.csv) files. These files can then be used off-line for investigations on inclusions or for research and development of new methods or algorithms for instance. They can be displayed graphically with the Spark-DAT viewer integrated in OXSAS, a very useful tool that shows sparks diagrams and intensity distributions, and helps searching coincidental peaks, set-up your inclusion analysis program and refine its parameters. They can also be used as input for third party programs.



New algorithms

Our company continues to develop new and improve existing algorithms. These are available to the existing users together with OXSAS upgrades.

Conclusions

The optional Spark-DAT methods available with the ARL iSpark 8860 and ARL iSpark 8880 metals analyzer increase the versatility of the instrument. From routine use to research, Spark-DAT methods provide quick, simple and cost-effective solutions for inclusion analysis in the aluminum industry. Among all the inclusions analysis methods available today for the aluminum industry, the Spark-DAT methods are the fastest.

The simplest Spark-DAT methods allow ultra-fast on-line counting of inclusions, identification of their composition and qualitative size classification in a time ranging from several seconds to a couple of minutes. This makes it highly effective for controlling inclusions during aluminum production.

The inclusion analysis can be combined with the standard analysis of elemental concentrations. The sample and its surface preparation, as well as the instrument maintenance and consumables, are equivalent compared to a standard OES instrument. This means extremely low operation costs compared to the other inclusions analysis techniques that require dedicated instruments. In addition, the ability to obtain elemental analysis information and inclusion contents with a single OES instrument greatly reduces investment costs.

To know more on ARL iSpark Series, visit www.thermoscientific.com/ispark

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