

DETERMINATION OF SOLUBLE AND INSOLUBLE COMPOUNDS IN METALS WITH SPECTROLAB

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Abstract. Spectrochemical procedures (PDA) and (PIMS) are fast and allow other elements to be determined simultaneously. A prerequisite for a reliable determination of various aluminum contents (ALT, ALO, and ALS) is the uniform distribution of insoluble aluminum (ALO). This condition is most easily fulfilled with sub-lance bomb samples and with samples from finished continuous-casting; with immersion samples of the lollypop type, this is not always the case. The PDA method requires special electronic equipments and is expensive. PIMS has successfully tested the soluble/insoluble determination of aluminum, titanium, boron and calcium. It can be implanted in all Spectrolab using Micro 5 data processing system. Chemical methods (taking ALS into solution by chemical or electrolytic means) will not determine the ALO part, are slow for routine analysis and require additional equipment and labor.

Key words: soluble, insoluble compounds, spectrolab, aluminium compounds spectrochemical procedures, titanium, boron, calcium.

1. INTRODUCTION

In the steel industry, aluminum can be found be as the most important de-oxidizing agent. During the process of micro-alloyed steels, aluminum is added as alloying element to promote the formation of aluminum nitride in order to improve the deep-drawing. In consequence, aluminum can be found in steel as metallic aluminum and (so-called soluble aluminum), aluminum oxide and aluminum nitride. Metallic aluminum and aluminum nitride can be dissolved in acid and so this part is called acid soluble aluminum or simply soluble aluminum. During the steel production process, it is important to have a measure of the level of the soluble aluminum in steel. The response time between the sampling and the reporting of the analytical result must be short in order to apply the requested corrections, meaning that a fast analytical procedure is required.

The first trials to apply optical emission spectroscopy to the analysis of soluble aluminum were run during the sixties. In 1961 it was discovered that the presence of manganese sulphide inclusion lead to an enhancement of the analytical

signals of manganese and sulphur. This comes from the fact that the spark at the beginning of the analysis preferentially attacks the inclusions. The same observation was later made for aluminum oxide inclusions [1]. Boron is used as an additive to increase the hardness of steel or to form boron nitride that reduces the content of dissolved nitrogen and increases the resistance of steel to ageing. Discharges in an Argon atmosphere preferentially attack inclusions in a metallic surface. This effect is not primarily influenced by the sample preparation method used. Finishing with different grit sizes, milling, or turning gives similar results. Neither the type of inclusions nor their melting/boiling points have a bearing; low-melting Pb droplets in steel or Pb sulphides in free-cutting steel show these preferential attacks as well as high-melting point non-volatile aluminum-or zirconium oxides.

To be more specific, it is not the inclusions that are attacked but the edges between the inclusions and the metal. This is due to the higher electrical-field strength at these points. As a matter of fact, the ignite discharge alone (without power discharge) also prefers these edges which seems to hint at a higher field electron-emission. Discharges against the edges (due to higher electrical field strength) are of the diffuse type! The corresponding intensities are undefined. The function of the measured spectral intensity is different for the precipitated elements (or compounds) than for the base element (Fe in steel) and the elements in solution. The principle is illustrated in Fig. 1. During the sparking-in time, ST,

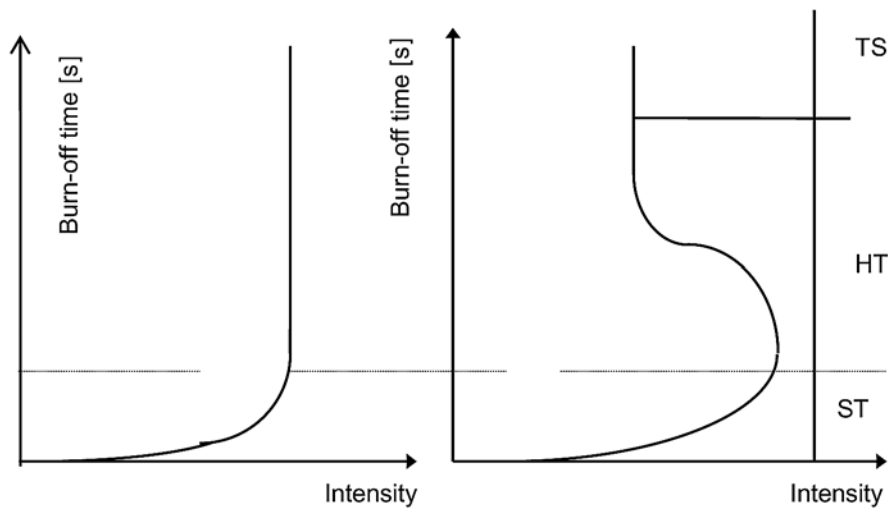


Fig. 1 – The dependence of intensity by burn-off time with medium-voltage discharge for steel in Ar. ST = sparking in time = $f(C_i, \Phi I)$; HT = homogenization time = $\varphi(C_i, \Phi I)$; TS = time for stationary state = $\gamma(C_i, \Phi I)$; C_i = concentration of inclusions; ΦI = diameter of inclusions, $TS = ST + HT$.

the edges of the inclusions at the very surface are attacked by so-called diffuse multi-burn spot discharges. Then the concentrated single-burn spot discharges will penetrate the sample to a certain depth (30–50 μm , depending upon heat conductivity and discharge energy) and remit the sample in the discharged area. Assuming the discharge hits a volume with inclusions, and then the concentration of the inclusions in the discharge crater is higher than the bulk analysis of the inclusions. Thus, as long as the inclusion sizes are small in comparison with the sizes crater, elements in form of inclusions show burn-off effects that are expressed in form of a peak during homogenization time. The homogenization time HT leads to the stationary state TS.

The inclusion sizes over the entire discharge area are then reduced ($\leq 0.1 \mu\text{m}$). The inclusion sizes are now very small compared to the crater sizes. The spectrometric signal is now independent of the binding form of the analytic element. Some years ago this was confirmed by carrying out the following test. A steel sample (0.03% S; 1.5% Mn) (unrolled) contained inclusions of MnS of 5 μm diameter. This sample was showing a large burn-off effect for S with a peak that was at maximum 5 times higher than the intensity in the stationary state. The time needed to reach the stationary state was about 20 s using the HEPS-technique [2, 3]. This HEPS technique (HEPS-High Energy Pre-Spark) can be demonstrated when looking at the sulphur intensity curve in an iron Base. Fig. 2 a shows S burn-off curves for steel samples with identical sulphur concentration (0.25%) but different inclusion size of MnS with and without a combined discharge.

The times (TS) up to the stationary state with discharge parameters 10 μF , 6 Ω , 120 μH , 800 V, 50 Hz (without combination) are as follows:

| | | | |
|-------------------------------------|------------------------------|------|-----|
| Remitted sample | 2 μm ϕ MnS | 100s | (A) |
| Cast sample | 3–5 μm ϕ MnS | 150s | (B) |
| Sample from a semi-finished product | ~20 μm ϕ MnS | 250s | (C) |

The interrupted burn-off curves were obtained by sparking with 50 μF , 3 Ω for 20 s and subsequently recording the sulphur intensity with 10 μF , 6 Ω to check the state obtained in burn spot (combination). With this method the times up to the stationary state are:

| | | |
|-------------------------------------|-----|-----|
| Remitted sample | 20s | (A) |
| Cast sample | 40s | (B) |
| Sample from a semi-finished product | 60s | (C) |

From the burn-off curve for the semi-finished product consisting of free-cutting steel (Fig. 2) two sparking phases are recognizable. During the first phase lasting approximately 20 s inclusions in the surface are attacked by the diffuse discharges. The discharge branches produce shallow crater depth. Attacked and vaporized sample quantities are not small but the intensity is low because of the low plasma temperature. The intensities of the base element and the elements dissolved in it are low. The phase up to the intensity peak for the inclusions is called

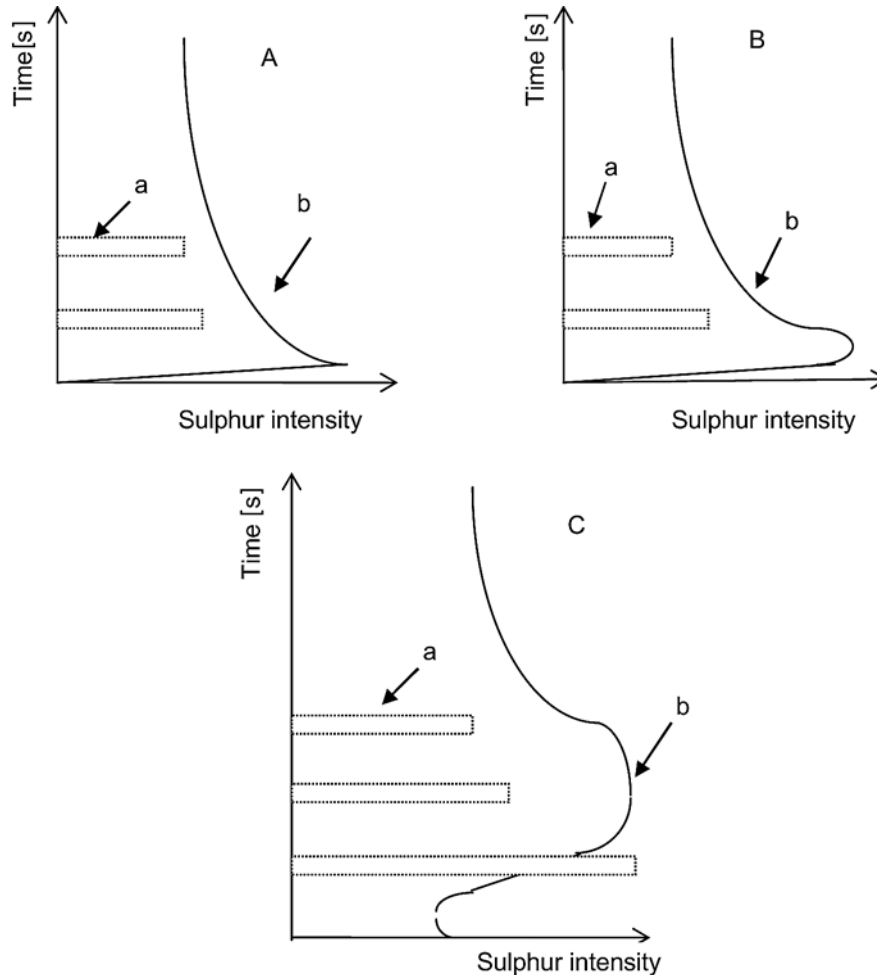


Fig. 2 – S burn-off curves without (b) and with (a) combined discharge with different MnS inclusion size (0.25% S in steel): A - MnS diameter = 2 μm , $T_{sb} = 100$ s, $T_{sa} = 20$ s; B - MnS diameter = 3–5 μm , $T_{sb} = 150$ s, $T_{sa} = 40$ s; C - MnS diameter = 20 μm , $T_{sb} = 250$ (s), $T_{sa} = 60$ s.

“sparkling-in time”. At the end of the sparking-in time all inclusions at the sample surface in the burn spot have been broken down and the intensities of the base element and the elements dissolved in it are constant.

The second phase is the “homogenization time” during which the remitting process (micro-fusion) takes place. Discharges are concentrated with one single cathode point of attack and great crater depth. It is assumed that the stationary state has been reached when each point at the sample surface in the burn spot area has been hit by at least one concentrated discharge (deep melting). Local overheating occurs at the points of impact; the inclusions vaporize faster. When a layer

thickness has been “remitted” which is identical with the penetration depth (crater depth), local overheating is no longer able to lead to spontaneous vaporization of inclusions. The sample is gradually remitted in the burn spot area point by point and there is no point in time where one entire layer is liquid.

After the sparking-in time (with cast sample it is short when compared to the homogenization time) discharge impact points are distributed over the surface. There are more impacts in the burn spot centre than on the outside, *i.e.*, discharges hit on already homogenized areas. If each discharge were to hit a “virgin” surface, burn-off curves for included elements would look as those shown in Fig. 3.

This applies on the assumption that a single remitting process leads to the inclusion being “dissolved”. Since the dissolution process takes time, it is proportional to quantity, size and kind of the inclusions. When one traces the actual curve “a” (not each discharge hits a fresh point) and the theoretical curve “b” (as if each discharge were to find a fresh point) in a burn-off diagram, then it should look like Fig. 4. Sample of different structure show intensities identical after pre-sparking for approx. 20 s. After this time any structural effect due to different cooling is eliminated. Measurement with a microprobe shows that it is due to enrichment in the burn spot.

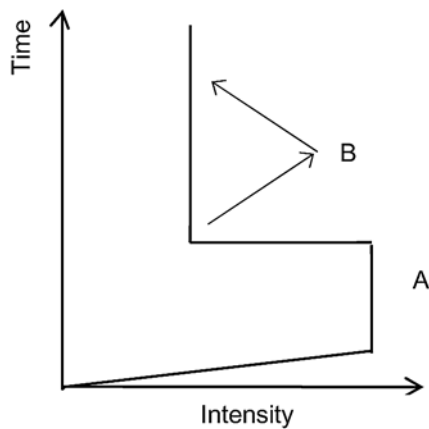


Fig. 3 – Burn-off curve sharp for inclusions if each discharge during the homogenization time were to find a fresh point: A) each discharge finds a fresh point; B) all points are homogenized and none of the discharges can find a fresh point.

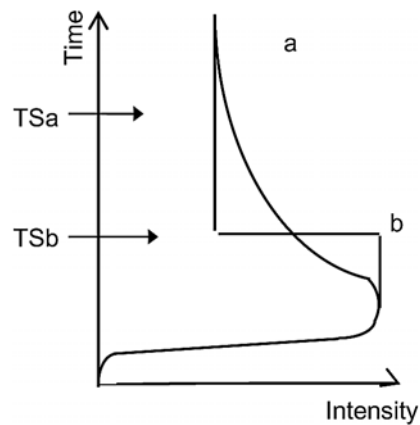


Fig. 4 – Actual (a) and theoretical (b) shape of the burn-off curve for inclusions.

The end of the homogenization time is the stationary state where the intensities of all elements are constant. Pre-spark time is the sum of sparking-in and homogenization time [3, 4].

2. EXPERIMENTAL

In this paper we describe an experiment using spark excitation to determine the soluble and insoluble aluminium and boron in steels. Soluble and insoluble aluminium in steels can now be determined quickly and accurately with Spectrolab's latest methodology, PIMS. The equipments used at the ISPAT-SIDEX laboratory to determine the chemical composition of the metallurgical products are Spectrometers from SPECTRO ANALYTICAL INSTRUMENT (SPECTRO) firm and APPLIED RESEARCH LABORATORIES (ARL) firm. Spectrometer is used for the analysis of most metals, including iron and steel, as well as aluminium, copper, nickel and other nonferrous metals and their alloys. Spectrometer is indispensable in our day-to-day life. Spectrometers do their work silently, but the effects of what they do are with us everywhere.

The SpectroLab is a simultaneous spark emission spectrometer for the analysis of Fe-, Al- and Cu-based alloys. The principle of the analysis method is optical spark emission spectrometry. Sample material is vaporized by a spark discharge. The atoms and ions contained in the atomic vapour are excited into emission of radiation. The radiation emitted is passed to the spectrometer optics where it is dispersed into its spectral components. From the range of wavelengths emitted by each element, the most suitable line for the application is measured by means of a photo multiplier tube.

The radiation intensity, which is proportional to the concentration of element in the sample, is recalculated internally from a stored calibration curve and shown directly as percent concentrations. For the analysis, the prepared sample is placed on the spark stand and the starting button is pressed. The analysis procedure takes about 30 seconds.

Fig. 5 shows a schematic diagram of a multi-optic system with four optical systems.

Radiation taken off from plasma for the individual spectrometer optics systems is carried out by light-guides or directly. Spectrolab can include as many

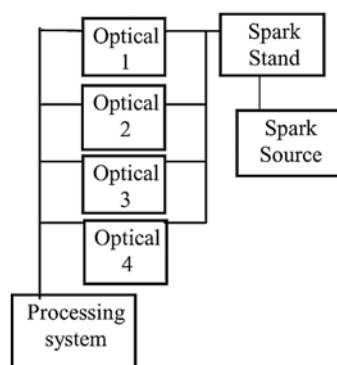


Fig. 5 – Schematic diagram of: Optical 1 – UV, max. 120–220 nm; Optical 2 – Air, max 220–780 nm; Optical 3 – Air, max 220–780 nm; Optical 4 – Air, max 220–780 nm.

as four spectrometers in a single system; one UV and up to three air spectrometers. The air path spectrometers view the light emission with fibre optics at different areas of the discharge. For wavelengths of less than 200 nm, measurement is carried out by special means. Optical emission spark analysis is by far the most widely used, industry accepted technique to provide chemical analysis for alloying and tracing elements in metals, [5–8].

RESULTS AND DISCUSSION

Optical emission spectroscopic methods are based on the assumption that vaporization of the sample constituents is proportional to the mean chemical composition, that the composition of plasma is proportional to that of the sample. From the change in time of the intensities of the spectral lines (burn-off curves) it can be seen that this assumption is not always correct.

Discharge in Ar initially attacks inclusions because there are high field intensities at the boundaries between inclusions and metal so that electron emission is promoted by field emission.

Fig. 6 shows burn-off curves with medium-voltage discharges for Al 3961.5 Å in air and argon for steel samples with identical aluminium but different Al₂O₃ concentrations. Burn-off curves in air are stable after the spark has been ignited; in argon they show a preferred attack of Al₂O₃ [4].

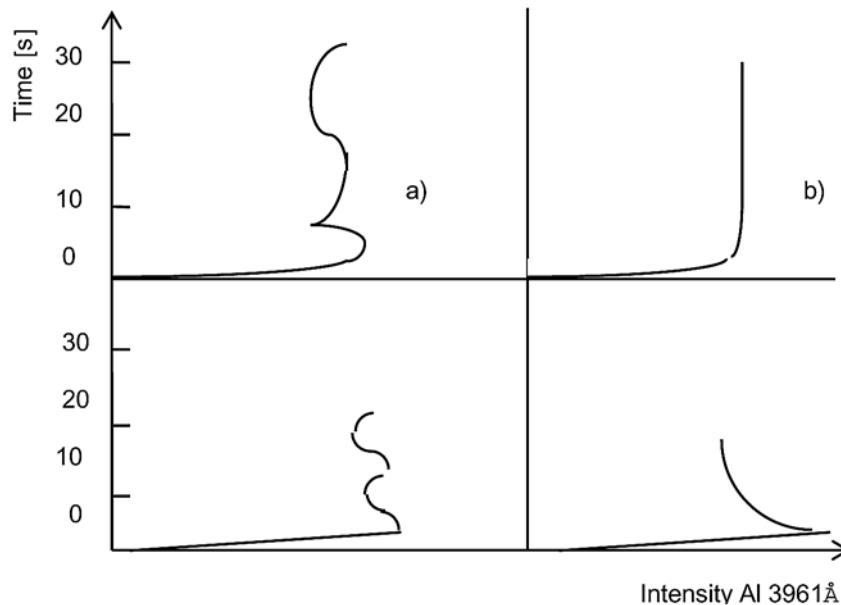


Fig. 6 – Burn-off curves Al 3961.5 Å with medium-voltage discharge in a) air and b) argon for steel; top: elemental aluminium; bottom: aluminium partially in form of Al₂O₃.

In the example given the intensities are independent of the Al_2O_3 concentration after approx. 30 s; that is the stationary state the intensities are proportional to the mean sample composition and free of effects due to different kinds of bond, inclusion size (the upper limit is dependent on the inclusion type, its melting-and vaporization point) and structural states. The stationary state has been reached when the intensities of all elements are independent of the burn-off duration. Inter-element interactions in plasma due to changes in plasma temperature caused by third partners are not affected.

Soluble and insoluble aluminum in steels can be determined with the PDA and PIMS methodologies.

Pulse Discrimination Analysis (PDA). When the discharge hits Al_2O_3 inclusions, and when these inclusions are at the very surface, low Fe intensities and undefined aluminum intensities are obtained (diffuse discharges) and high aluminum intensities are obtained. All single aluminum signal amplitudes are measured. Where the corresponding Fe intensities are within a narrow predetermined range (concentrated discharge) they are recorded. If the accepted aluminum pulses are plotted, two different populations of data will develop: one for ALS and for ALO.

Remarks:

1. The first population will represent ALS only inasmuch as the discharge hits a new spot that has not been homogenized by one or several previous discharges. Only then will this spot not yield a peak upon variation of finely dispersed Al_2O_3 in the crater region as is the case in the stationary state.

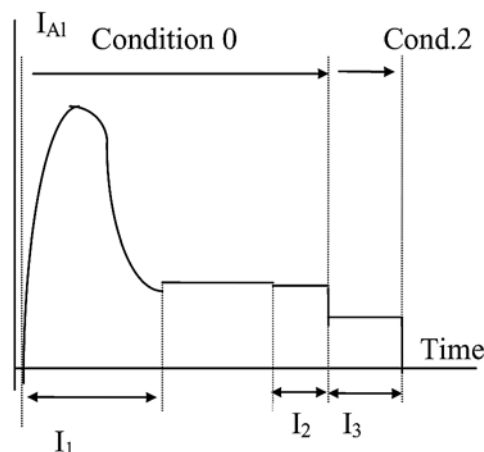
2. Alt is computed from the median Alm of both populations and a coefficient develops. It is not clear why one does not simply calculate $\text{ALT} = \text{ALS} + \text{ALO}$, since ALS and ALO are supposed to be measured.

3. Instrumental costs are high, for the method reported, since special electronics is required.

Peak Integration Method (PIMS). The burn-off curve of the precipitated elements as well as the intensity distribution of the single discharges indicates that all signal amplitudes above a certain level are associated with ALO. That level is, for the burn-off curve, the intensity of the stationary state. The intensity is then independent of the binding form, a fact for which there is much practical evidence. If ALO is present, the burn-off curve has a peak; in the absence of ALO, there is no such peak. This was confirmed for ALT to 0.25% and $\text{ALO} \geq 0.001\%$ [2].

Fig. 7 shows the evolution of the aluminium signal from the start of the analysis. The signal first increases to peak due to the presence of the oxide inclusions, then, it is assumed, the oxide particles are broken down so that they can be considered to be “dissolved” in the metal. After some time the signal stabilizes when all the particles have been broken down.

Fig. 7 – Evolution of the aluminum signal from the start of the analysis.



Following this discovery, the peak integration method (PIM) was introduced at SIDEX in 2000. In this method the first period of integration I_1 is related to the aluminium oxide content of the steel, while period I_3 gives the total aluminium content of the steel.

We have the following relation:

$$Al_{tot} = f(I_3) \quad (1)$$

$$AL_{sol} = f(I_2/I_1) \cdot AL_{tot} \quad (2)$$

Using modern excitation conditions (HEPS) and data processing facilities one can measure the peak intensities as well as the intensity in the stationary state. The stationary state gives an accurate signal in relation to the peak intensity relating to the calibration of the soluble aluminium ALS. The insoluble part can be calculated as the difference: $ALO = ALT - ALS$ [9].

Aluminium oxide inclusions were observed when taking lollypop samples from purged ladle. Samples from steel melts must be taken with immersion samplers and not with a spoon and a meld. The latter leads to oxidation during Al pouring. With mild steel, there is a risk of contamination from the abrasive grin. Note: Due to the slower cooling-down of sub-lance bomb samples the solidification pushes Al_2O_3 towards the residual melt, resulting in reduction at the base and in enrichment at the top. With lollypop samples the solidification is faster and the Al_2O_3 (and coagulated) inclusions remain in place [10].

Soluble and insoluble aluminium in steels can now be determined quickly and accurately with SPECTRO and ARL latest methodology, PIM. Table 1 shows no significant influence from the sample preparation on the PIMS-results (with SPECTRO). Samples were milled and ground with the 40, 60, 80 grit paper. Some finishing papers were found to contain Al_2O_3 as an abrasive or bonding agent.

After several investigations we found a grinding paper that gives no contaminations for aluminium. Milling will produce a contamination-free surface. The eye in milled surfaces can spot clusters of aluminum oxide. Samples with Al_2O_3 clusters will yield random aluminium values when the clusters are sparked. It was noticed that big immersion (sub-lance bomb) samples systematically gave lower aluminium values than smaller sample shapes (like lollipop samples). This is plausible because of the homogeneous ALO distribution.

Table 1

Comparison of PIM results with different sample preparations

| Sample | Element | Etalon Concentration (%) | Ground 40 | Ground 60 | Ground 80 |
|--------|---------|--------------------------|-----------|-----------|-----------|
| 11 | ALT | 0.014 | 0.014 | 0.014 | 0.014 |
| | ALS | 0.010 | 0.009 | 0.009 | 0.009 |
| | ALO | 0.004 | 0.005 | 0.005 | 0.005 |
| 22 | ALT | 0.025 | 0.025 | 0.025 | 0.025 |
| | ALS | 0.017 | 0.017 | 0.017 | 0.017 |
| | ALO | 0.008 | 0.009 | 0.009 | 0.009 |
| 33 | ALT | 0.029 | 0.029 | 0.029 | 0.029 |
| | ALS | 0.021 | 0.020 | 0.020 | 0.020 |
| | ALO | 0.008 | 0.010 | 0.010 | 0.010 |
| 44 | ALT | 0.025 | 0.026 | 0.026 | 0.026 |
| | ALS | 0.015 | 0.014 | 0.014 | 0.014 |
| | ALO | 0.010 | 0.009 | 0.009 | 0.009 |
| 55 | ALT | 0.059 | 0.060 | 0.060 | 0.060 |
| | ALS | 0.041 | 0.040 | 0.040 | 0.040 |
| | ALO | 0.018 | 0.019 | 0.019 | 0.019 |

Table 2 shows a reproducibility test for $Alt = Al_{total}$, $Alo = Al_{undissolved}$ and $Alm = Al_{metallic}$ made on a Spectrolab for etalon no. 33, $Alt = 0.029$, $Alm = 0.021$, $Alo = 0.008$.

Table 3 shows a comparison of analytical results for Al. The nominal values are wet chemical figures, the figures listed below ARL and SPECTRO are figures from the spectrolab.

The agreement is very good. The following graph shows the results of the analysis of soluble aluminum on 15 production samples by the different methods: PIM and the reference method of atomic absorption (AAS). The comparison shows a very small bias between the results, confirming the good agreement between the two methods (Fig. 8).

The following result was obtained on some certified samples by the PIM method. They are typical of what can be obtained by such methods.

Soluble and insoluble boron in steels can now be determined quickly and accurately with ARL latest methodology, PIM. The boron nitride can be found as

Table 2

Reproducibility test for Alt = Al total, Alo = Al undissolved and Alm = Al metallic.
(Etalon no. 33: Alt = 0.029, Alm = 0.021, Alo = 0.008)

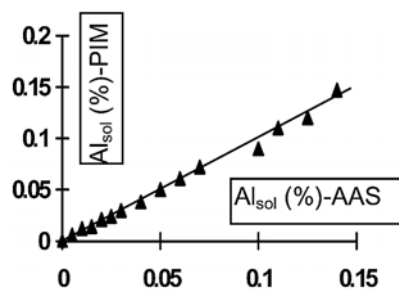
| Experiment | Al _{total} , Alt (%) | Al _{metallic} , Alm (%) | Al _{undissolved} , Alo (%) |
|------------|-------------------------------|----------------------------------|-------------------------------------|
| 1 | 0.0289 | 0.0212 | 0.0077 |
| 2 | 0.0292 | 0.0209 | 0.0083 |
| 3 | 0.0289 | 0.0211 | 0.0078 |
| 4 | 0.0279 | 0.0201 | 0.0078 |
| 5 | 0.0295 | 0.0208 | 0.0087 |
| 6 | 0.0288 | 0.0211 | 0.0077 |
| 7 | 0.0292 | 0.0211 | 0.0081 |
| 8 | 0.0287 | 0.0199 | 0.0088 |
| 9 | 0.0294 | 0.0220 | 0.0074 |
| 10 | 0.0291 | 0.0213 | 0.0078 |

Table 3

Comparison of analytical results for Alt, Alm, Alo with different spectrometer

| Sample | Alt | Alm | Alo | method |
|--------|-------|-------|-------|---------|
| 11 | 0.014 | 0.009 | 0.005 | ARL |
| 22 | 0.025 | 0.017 | 0.008 | ARL |
| 55 | 0.060 | 0.040 | 0.020 | ARL |
| 77 | 0.045 | 0.033 | 0.012 | ARL |
| 11 | 0.015 | 0.010 | 0.005 | SPECTRO |
| 22 | 0.026 | 0.015 | 0.011 | SPECTRO |
| 55 | 0.059 | 0.037 | 0.022 | SPECTRO |
| 77 | 0.044 | 0.036 | 0.008 | SPECTRO |

Fig. 8 – Comparison Alsol% OE-PIM with Alsol AAS.



aggregate formed by precipitation. As for the oxide particles, the spark at the beginning of the analysis preferentially attacks these aggregates. This phenomenon leads to the same determination method as for aluminium. Therefore, the same calculation formulas are implemented in the software using PIM [4].

Table 4

Results obtained on certified samples

| Sample | Element | Etalon concentration (%) | Obtained concentration (%) |
|--------|----------------------|--------------------------|----------------------------|
| 81 | B _{tot} | 0.61 | 0.63 |
| | B _{sol} | 0.55 | 0.56 |
| | B _{nitride} | 0.06 | 0.07 |
| 82 | B _{tot} | 0.48 | 0.496 |
| | B _{sol} | 0.43 | 0.45 |
| | B _{nitride} | 0.05 | 0.046 |
| 83 | B _{tot} | 0.23 | 0.24 |
| | B _{sol} | 0.19 | 0.22 |
| | B _{nitride} | 0.04 | 0.02 |
| 84 | B _{tot} | 0.13 | 0.15 |
| | B _{sol} | 0.09 | 0.107 |
| | B _{nitride} | 0.04 | 0.043 |
| 85 | B _{tot} | 0.10 | 0.095 |
| | B _{sol} | 0.07 | 0.085 |
| | B _{nitride} | 0.03 | 0.01 |
| 85 | B _{tot} | 0.41 | 0.45 |
| | B _{sol} | 0.34 | 0.37 |
| | B _{nitride} | 0.07 | 0.08 |

4. CONCLUSION

The PIM method is an option to the low alloy steel program which allows the determination of the soluble concentration levels of aluminium and boron in steel. The method does not require a special sequence or special condition; it is integrated into the normal process of analysis so that no extra time is needed over a conventional analysis. The time between the start of the analysis and the reporting of result is about 20 s. This is much shorter than the time needed to process the sample through a classic wet chemistry analysis that takes minutes to complete. It requires only a simple instrument and does not need special skills from the operator. It replaces a costly and lengthy procedure by wet chemistry.

The method is fast and the accuracy is, in most cases, more than satisfactory for process control requirements.

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