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From now on in the iron and steel industry, on-line analysis will be a necessity for reasons of metal quality, productivity and economy. To achieve this aim much research is taking place in the world and this paper is intended to summarize what has been done recently in Europe.

I. SPECTRAL ANALYSIS OF LIQUID METAL

For analysts, the direct analysis of liquid metal has been a dream. If possible it would reduce costs, shorten delays and eliminate all sampling problems, provided such an analysis is precise and accurate. In this field two attempts have to be mentionned.

1) Sparking of liquid metal

Particularly taking into consideration its continuous steelmaking process IRSID, in France, performed a feasability study at the laboratory level, sponsored by the European Community for Steel and Coal (ECSC) (1).
The experimental outlay was the following:
- a r.f. generator of 20 kw,
- a fusion unit with an alumina crucible permitting the melting of up to 3 kg of metal, enclosed in a water cooled gas tight housing,
- an optical system to transfer the light from this assembly to the entry slit of the spectrometer,
- a contact anode dipping in the metal, made of a molybdenumalumina cernet itself contained in an alumina tube. The optical system disposes of an annular mirror permitting a 4 fold magnified view on a screen and a rotatable mirror for adjustment of the plasma observation.

a) Spectrographic study

During a first step a quantovac ARL 31.000 spectrometer was modified by adaptation of a film holder where the vertical movement allows for 20 exposures. When an unipolar low voltage spark was applied to steel above 1350°C only a continuous ionisation of argon gas was observed. Even without sparking a potential due to thermoionisation was noticeable. Hydrogen could not be chosen for security reasons but pure nitrogen permitted the recording of bright spectra. The gap between the pure iron electrode and the bath must be under tight control, particularly for C,P,S because of the heterogeneous structure of the spark plasma. Spectra were recorded during 10,20 or 30 sec.

b) Spectrometric study

The second step consisted in the use of a Sequantometer ARL 33.000 with the same characteristics as the previous instrument. In this case line intensities were ratioed in respect to iron lines of the same spectral origin as the lines measured. To modify the bath compositions two techniques were applied :
- removal of liquid metal by suction and addition of alloys,
- removal of liquid alloy by suction and dilution by pure iron.
Signal intensities have been traced up to 8 hours. They are sensitive to deposits on lenses, gap modifi-cations and electronic drifts but no bath temperature influence was noticed between 1400 and 1600°C. After a preburn of 30 sec., stable signals allowed for repeatability studies concerning 17 elements and 2 iron reference lines. Small slag particles on the surface are attracted into the spark impact area modifying the geometry as well as the optical response. Any slag must be avoided.
Under such conditions RSD's between 0.7 and 2% were observed for C,Mn,P,S,Si,Al,Ni,Cr,Mo,Sn for carbon and low alloy steels. In all cases eventual gap variations have been compensated for by mobile mirror adjustments.
This work demonstrates that such an analysis is possible with a precision only slightly lower than by classical OES and bright spectra were observed even for carbon.

2) Atomisation of liquid metal and subsequent excitation

In the United Kingdom BSC aimed at direct metal analysis in a tilted basic oxygen converter with the financial support of ECSC (2). The idea was to use a lance with a disposable incorporated atomiser to produce an aerosol transported under argon to a plasma excitation OES. This atomiser comprises a protection cap, aluminium for de-oxidation and it is immersed into the metal for 10 sec. The liquid metal passes through a silica tube and is atomised by an argon flow at sonic velocity through an annular gap. The cooled droplets are transfered to a settling chamber to eliminate particles above 50 μm.
The fines are conveyed through a 30 m long pipeworks for collection. It was shown that there was no significant difference in composition before and after transportation at Ebbw Vale works, so no contamination.
For the analysis two excitation systems were tested, linked to a conventional UV spectrometer:
a) a plasma jet with a 30 A d.c. arc with tungsten electrodes energysed by a modified welding generator of 0.7 KW. The powder was injected co-axially into the plasma and the emitted spectra observed at right angle,
b) an ICP torch operated at 6 MHz with a power of 15 KW, a hole being punched into the plasma by an argon stream of 3 l/min. carrying the sample. During the lance design study oil contaminations, high calcium contents due to slag pollution could be eliminated and comparison analyses were performed using lollipop samples attached to the lance. The success rate for 5 g powder sampling was 80%. Such comparisons for 24 runs led to linear regression coefficients between 0.85 and 0.98 for C,Mn,S,P but in Port Talbot works it was noted that 70% of carbon results were too low, showing that the de-oxidation problem had not been entirely overcome. Using a mixing chamber in the lance the carbon loss was 0.0005% at levels between 0.01 and 0.03%C. The repeatability coefficients of variation were 0.6-0.9% for C,Mn and 1.3-2.5% for Si,S,P. With an argon methane mixture this coefficient was 0.22% for carbon using the ICP

excitation. Feeding of both excitation devices with powder samples has been studied by fluid bed and gravity. The following conclusions resulted from this work :
- good operation of lances and measurements,
- the powders produced are chemically representative of the melts,
- these powders can be transported to a laboratory 30 m away within 10 sec.,
- critical parameters for powders are the grain size distribution and metallurgical variatious within the particles,
- the overall precision observed was less than that of classical OES, not sufficiently high for production control.

II. ALUMINIUM PHASES ANALYSIS IN STEEL

The knowledge of dissolved and precipitated aluminium is fundamental now for metallurgists, especially in relation with continuous casting. A very short response time is needed, eliminating most chemical methods. Also the chemical shift observed with XRF lines is too small to be usable by industrial spectrometers.

1) Optical emission spectrometry

Japanese research had previously shown the way and led to Pulse Discrimination Analysis (PDA)(3). Sponsored by ECSC (4) IRSID focused only on aluminium and tried to simplify electronics thinking that due to the progressive elimination of the alumina inclusions by sparking it should be possible to profit from burning curves. In practice, using a 100 Hz source, 400 sparks are emitted within 40 sec., this period being divided in 4 equal sequences. During sequence I, the signal integration concerns mostly alumina whereas sequence IV permits the quantifying of dissolved Al only and the whole cycle is related to the total Al.
This is based on the SUMITOMO demonstration (5) that the sparks erase alumina inclusions and that could be confirmed by SEM observations. Spark source parameters were :
$C = 3\ \mu F$ $R = 2,2\ \Omega$ $H = 20\ \mu H$ $V = 400\ V$

The results observed agree well with those relevent to selective dissolution followed by AAS determination. Following repeatability standard deviations have been observed :
Alp: 7 ppm   Ald: 11 ppm   Alt: 21 ppm

In fact the PDA and the present work demonstrate that the usual heavy pre-sparking eliminates the looked for inclusions so that what is called total Al in classical OES in fact has to be assimilated to dissolved Al. As well PDA or sequantial integration, both using no pre-sparking and smooth sparking conditions, shed new light on all OES analyses of steel. The price to pay for that is to again have to handle structural effects of steel previously eliminated by heavy pre-sparking. In other words, using these new techniques, analysts must calibrate their instruments for not too many different steel varieties in one run.
The question then arises : how about AlN ?
Using the same samples where AlN was completely dissolved or precipitated in the matrix by thermal treatment it seems that AlN is taken in account with dissolved Al for following reasons :
- AlN is not as good an isolator as alumina, thus it cannot be eroded,

- the grain size of AlN is much too small in respect to alumina inclusions.
What will be studied now at IRSID are the properties, in this field of spectrometry, of mixed oxidic inclusions especially when steels are calcium treated. From the point of view of liquid steel sampling for Al phases analysis it must be stressed that lollipop samples are relatively heterogeneous and that best results are observed with bomb type samples.
A spectrometer incorporating this sequential integration Al phase analysis will be marketed now by Jobin-Yvon.

2) DHS - 1200 sampler

The Dillingen works (W. Germany) tried to find a direct access to dissolved Al by developing a specific sampler (6). The basic idea was to achieve the alumina decantation in a mold by retarded solidification. It was also intended to eliminate any oxygen in the mould before sampling. This device is now marketed by Soled (France).
Using a thick refractory wall the temperature loss is slowed down. The lid of the mould presents a central boring to adjust filling speed. The relatively important sampling volume contains a magnesium strip fixing all gaseous oxygen by burning at the beginning of the filling process. It also contains a Zr or Ti strip to eliminate any chemically bound oxygen from the inner surface or any parasitic oxygen coming from the refractory when getting hot. These last metals are mostly found on the bottom of the solid sample. After cutting off the lower half of the latter the metal is submitted to OES analysis. This method does not allow for alumina determinations but for dissolved Al good agreement is observed with chemical analysis, the standard deviation being 6,5 ppm at a level of 420 ppm for calcium treated steels.

III. SUB-LANCE SAMPLING

While sub-lances are used in a variety of European steelworks particular studies took place in Scandinavia.

1) AOD converter

At Avesta (Sweden) 5 Scandinavian steel producers collaborated using an Atlas Copco (France) equipment Whereas equipments used in USA and Japan were estimated in 1981 at 1.2-2.0 US $ this installation costs only 90.000 US $ and needs less space.
Before the reduction step Spemis (Soled-France) samplers are used with a yield of 95%. After reduction a Rescon (Sweden) sampler is used, made of refractory to keep the metal liquid for 30 sec. During this delay slag separates. The conical sample weight is 500 g and the efficiency 95%. In a report (7) much analytical evidence is given.

2) Other vessels

A 5 year study also concerned automatic sampling in converters, electric and ESR furnaces, ladles, continuous casting moulds and temperature measurements. The equipment is based on the CRM (Belgium) pneumatic outlay and Rescon samplers are used with a 99% yield (8).

IV. AUTOMATION OF NON METALLIC SAMPLE PREPARATION

Future on-line analysis will also involve oxidic samples like ores, sinters, slags, refractories, etc. To speed up the bead preparation for XRF analysis

various studies sponsored by ECSC have been carried out.

1) Preparation of only oxidic products

To dispose of a fast method without any heat, noise ore fume nuisance IRSID developped an automatic microprocessor controled device called Perl'X-2 delivering a bead within 3 to 5 minutes so as to allow the steelmaker to dispose of the analytical information in shop within 10 min. (9) Using a flux (grain size 100-500 µm) called Fluosid 21, marketed by ICPH (France), with following composition :

  lithium tetraborate : 75.6%
  lanthanum oxide : 20.9%
  boric anhydride : 3.5%

5 g of this flux are mixed with 0.3 g of sample and 2 to 3 mg of sodium iodide and added in a platinum alloy crucible with flat bottom.

The crucible is disposed in the coil of a r.f. generator delivering a power of 2.5 KW. During the fusion at 1200°C the coil is oscillated 30° around horizontal axis. For casting in a platinum dish, pre-heated by the same generator, the assembly is rotated automatically 150°. Finally the dish is cooled by a jet of cold air. The preparation standard deviations are very low, for example 0.13% at the level of 61% iron in an ore or sinter.

2) Preparation of samples containing reduced components

Products like dusts may contain metallic particles or carbon, lead, zinc etc. The programme of the Perl'X-2 also allows for a pre-oxidation step at about 500°C without oscillating for a few minutes before melting. In this case a flux made of 76% lithium tetraborate and 24% sodium nitrate is used. This automatic bead preparation device is marketed by Philips International and it is worthy to note that with one crucible 1500 up to 2000 beads can be melted.

3) Preparation of ferro-alloys and other products

Based on this instrument ARBED (Luxembourg) (10,11) developped a method to prepare beads with Cr, Mn, Mo, Nb, P, Si, Ti, V, W ferro-alloys, silico-manganese and -calcium, hard metals, oil refinery catalysts, lead and zinc dusts, bituminous shales, pyrites, used engine oils, copper alloys and even steels on a routine and referee basis. Using a nitrate mix for oxydation and lithium tetraborate as flux, disposed in the crucible in a particular way, beads of such samples can be prepared within 10 min. with very good results ($s_{prep.}$ = 0.14 at the level of 72% Si in a ferro-silicon).

The most important feature with Perl'X-2 is the possibility to perform absolute calibration using pure substances.

4) Automatic solution preparation

For ICP, AAS and chemical methods a fast solution preparation is needed. Thanks to an other ECSC grant IRSID has modified its Perl'X-2 (12). As strictly all the melt must be recovered here after casting, a glassy carbon crucible not wetted by the melt, is introduced into the platinum crucible, the carbon crucible being heated by conduction and radiation. Up to 15 samples can be prepared with one such crucible. The melt is automatically cast in water or an acidic solution, any splashing being prevented by a magnetic stirrer below the beaker. This device named Plasmasol will be marketed by Jobin-Yvon.

Recently these two instruments have been combined.

This new Sol'X, using its microprocessor, casts on request either a bead for XRF by tilting the crucible on one side or prepares a solution on the other side within 3 to 5 min., provided correct flux and crucible are used.

5) ICP lines atlas

As no such atlas was at hand, based on matrix bearing solutions, a ECSC grant permitted IRSID to establish an ICP lines atlas well adapted to applications in our industry (13). It covers the range 175 to 460 nm for 43 elements and references to interferences are given. Measurements were made with a 5 KW tuned line DURR generator at 50 Mhz and a ARL 35.000 monochromater equiped with an ultrasonic or a concentric flow nebulizer.

V. STEEL CONTROL WITHOUT SAMPLING

For rolled steel control and sorting a mobile OES spectrometer has been developped by Thyssen works in W. Germany with the financial aid of ECSC (14). The metal being surface ground, a pistol produces a powder via a d.c. arc. This powder is conveyed at 10 m through an argon flushed tube.

In a 7.5 t truck with a 18 kVA generator in a trailor, a ARL 31.000 spectrometer is located as well as argon bottles, air conditionning and computer facilities.

For excitation of the powder a capillary arc is used permitting an analysis within 30 sec. for 13 elements including carbon. Repeatability and accuracy compare well with those using samples in a classical laboratory. It has been shown that carbon is not transported by the powder but as CO and CO_2, the carrier gas containing 0.5% nitrogen and 0.03% oxygen.

The working parameters are the following :

- aerosol generator : intensity: 4 A, voltage: 30 V, argon flow: 2 l/min., gap: 1.5 mm, preburn: 25 sec., integration: 5 sec.
- capillary arc : intensity: 10 A, voltage: 50 V, argon flow: 1,4 l/min.

No pollution during powder transport was observed and after each analysis the transfer tube is argon flushed. For metallic elements iron ratios are used but for C,P,S direct intensities are computed. Limits of detection are 0.002 to 0.003% for S and P, 0.01% for carbon and the other elements Si, Mn, Al, Cr, Cn, Mo, Ni, Nb, Ti and V.

This mobile spectrometer is used inside Thyssen works as well as for remote control (500 km) of ingots, slabs, plates etc. For sorting 150 slabs could be controled within 4 hours. This technique is also invaluable for ingot and slab segregation studies at a multielement level. It has now been extended to high alloy and heat resistant steels with good results.

VI. FUTURE DEVELOPMENTS

On-line analysis of oxygen phases in steel would also be needed. OHTSUBO (15) demonstrated the HHE possibilities off line. With reduction fusion instruments like Leco 316 or Ströhlein Osamat 350 IRSID will investigate the potentialities when a temperature ramp is used. In the near future it would even suffice to dispose of a "finger print" analysis compared with a reference to allow for

a quick casting decision on the stage.
For a direct in-converter multi-element analysis using a laser, a study has taken place in Japan (16) and in the USA an investigation is starting. It would be very valuable to dispose of more information in this very promissing field for in-works-applications.
AAS is now common place. It would be worthwile to develope studies on electrothermal AAS using fast prepared solutions or better single chips to investigate the applicability of ETAAS to on-line analysis.

VII. CONCLUSIONS

Potentialities have been shown for direct liquid metal analysis, the Al phases determination reached an industrial level but more work is needed to better take in account structure effects. The automatic sample preparation reached a high level of development and control and sorting of solid steels has greatly improved. But it must be stressed that up to now no manufacturer has accepted to market this mobile spectrometer. This demonstrates that not all minds are ready to accept such new ideas.
Nevertheless, in Europe, as well as elsewhere in the world, it is clear that it is in-works as well as sponsored research - ECSC is a good example - that will permit not only the survival but also guarantee the progress and evolution of our iron and steel industry.

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