

Ferro-alloys analysis by Wavelength Dispersive X-Ray Fluorescence spectrometry

Didier Bonvin and André Kohler

Introduction

Ferroalloys are important materials in the specialty steel industry as their addition to molten steel in predetermined quantities produces steels with specific physical and chemical properties. It is therefore important to be able to analyze the ferroalloys to confirm compliance with their chemical specifications and allow precise additions in the ladle. In addition this analysis can be used as a control of the supplied materials for invoicing purposes. Analysis of ferroalloys are therefore carried out at least once a week and on each new supply. In view of the ISO 9000 certifications of many suppliers, there is a trend starting within the iron & steel industry to diminish the number of analyses done on ferro-alloys and to rely on the analysis certificates submitted by the suppliers.

There is a large variety of ferroalloys (Table 1) and their preparation for XRF analysis will vary depending on the hardness of the material and the demands in term of analytical precision and accuracy.

Table 1: Types of ferroalloys employed in the iron & steel industry

Fe-B	Fe-P	Fe-Mn	Fe-Si
Fe-Cr	Fe-Nb	Fe-Mn-C	Fe-Si-Mn
Fe-Cr-C	Fe-Ni	Si-Mn	Fe-V
Fe-Cr-Si	Fe-Ti	Fe-Mo	Fe-W

5.6.1 Sample preparation

Preparation of ferroalloys for analysis is not a simple task. Three main procedures can be employed.

a. Remelting with pure iron

This method allows to obtain a metal button by remelting the ferroalloy mixed with pure iron chips, in a high frequency furnace and through centrifugation of the melted metal. Crucibles are made of silica-alumina refractory material with a capacity of about 20 ml and molds of copper-beryllium are often used. The most important parameters to be controlled are the dilution ratio and the melting and casting times

and temperatures (ref. 1). Best results are obtained with dilution varying from ratios of sample to pure iron of 3:5 to 3:17 for the most difficult ones. Melting temperature are chosen between 1300 °C and 1900 °C with melting times of about 2 minutes. Fusing at these high temperature can involve the loss of some elements, namely Al and Ti. In some cases some Si pollution from the crucible can be incorporated in the liquid bath during fusion. The obtained disks look like thick coins and are polished with abrasive paper like steel samples.

Using the remelting method the grade element concentration of all the ferroalloys can be determined with tolerances of $\pm 0.2\%$ and $\pm 0.4\%$ (2 sigma) and the relative standard deviation values (RSD) for the minor elements are below 5%.

b. Pressed pellets

Ferroalloys are usually extremely hard and difficult to crush or mill, but this method is rapid and inexpensive. Grinding time and grain size must be strictly reproduced for best results. Typically the milled sample should pass through a 200 mesh sieve ($< 74\mu\text{m}$), but be retained by a 400 mesh sieve ($> 37\mu\text{m}$). Various binders are used, e.g. 10% methyl-cellulose or a solution of Elvacite added on top of the powder just before pressing at 20 to 40 tons.

Standard deviation of 0.1 to 0.15% around the calibration curve can be achieved for the major elements, while RSDs for minor elements are between 3 and 5%.

As the specimen preparation is the same for all ferroalloys a single analytical program can be built incorporating all of them (Table 2). This is a very handy starting point before refining the program into specific calibration curves for each type of ferroalloy in the quest for the best results.

The use of specialized synthetic multilayer crystals and the enhanced sensitivity of modern WD-XRF spectrometers allows to get much improved precision and limits of detection on elements which used to be impossible in the past. An element like boron can now be determined in ferro-boron prepared as pressed powder with good precision (Table 3).

Table 2: Typical repeatability for boron analysis in ferro-boron with WD-XRF
conditions: AX20 crystal, 30 kV, 100 mA, 10s counting time per run
instrument: ARL 9400 sequential spectrometer

Run nr.	Boron %
1	19.34
2	19.38
3	19.34
4	19.36
5	19.31
6	19.39
7	19.43
8	19.41
9	19.38
10	19.46
11	19.34
Avg.	19.38
Std. Dev	0.04

c. Fusion beads

In order to fuse ferroalloys with a flux and cast the resultant melt into a mold, the ferroalloy must first be converted to an oxide. Oxidation of ferroalloys by simple heating is possible but the reaction is exothermic and if done directly in a platinum/gold crucible considerable damage to the crucible takes place. Various methods have been proposed in the literature using muffle furnace or fusion machines (ref. 2,3,4,5). In some cases, $\text{Sr}(\text{NO}_3)_2$ is used as oxidant in others NaNO_3 with fluxes made of mixture of $\text{Li}_2\text{B}_4\text{O}_7$ and Na_2CO_3 . A recipe for Fe-Mo preparation proposes a flux made of CaCO_3 , NaCO_3 and $\text{Na}_2\text{B}_4\text{O}_7$, while a mixture of only CaCO_3 and $\text{Na}_2\text{B}_4\text{O}_7$ is used for Fe-V and Fe-Ti. Dilution can be as high as 1 to 35 sample to flux ratio, thus diminishing the matrix effects but also the intensities obtained on the XRF instrument, which can lead to difficulties with the trace elements.

One of the successful method (ref. 6) protects the platinum crucible during oxidation of the ferroalloys, completes the oxidation by chemical reaction with lithium carbonate (Li_2CO_3) and finally dissolves the oxidized ferroalloy in lithium tetraborate (LiT) flux. A protective layer of solidified LiT is formed on the inside walls of the crucible by melting a known mass of lithium tetraborate in the crucible at 1200 degrees C for 3 minutes. The protective layer is formed by removing the crucible from the furnace with tongs and rotating the crucible until the molten lithium tetraborate has solidified on the walls of the crucible.

The ferroalloy that is to be fused must be of fine particle size preferably less than 30 microns. The dried ferroalloy powder is added so as to form a thin layer in the base of the crucible. Oxidation of this layer of ferroalloy takes place in a furnace at 800°C with a free flow of air available to the interior of the furnace. After cooling, lithium carbonate is added so that it forms an even layer over the oxidized ferroalloy. The crucible is returned to the furnace at 800°C . The lithium carbonate melts at 620°C and helps to oxidize the ferroalloy and dissolve the oxidized ferroalloy. The crucible is transferred to a furnace at 1250°C where normal fusion takes place and the resultant melt is cast into a preheated mold to produce a glass bead. Whenever C content exceeds 0.1% a loss on ignition (LOI) correction must be done.

Major elements present deviations around the calibration curve of about $\pm 0.1\%$ while RSDs for minor elements are found to be better than 3%.

Table 3 : Calibration specification for ferroalloys and comparison of typical standard error of estimate for fused beads and pressed powders.

Element	Range [%]	Typical SEE [%] Fused Beads	Typical SEE [%] Pressed Powders
Nb	43.0 – 68.0		0.04
Si	0.01 – 91.0	0.37	0.30
P (high)	0.2 – 26.0		0.30
P (low)	0.01 – 0.30	0.005	0.02
Ti	0.50 – 37.00		0.20
Mn	0.1 – 90.00	0.24	0.40
Cr	53.0 – 74.00		1.20
V	0.1 – 81.00	0.17	0.40
Mo	59.00 – 76.00	0.86	0.90
Al	0.60 – 7.20		0.12

Dissolution in acids followed by drying and then fusion of the residue into a glass disk with suitable fluxes for presentation to the XRF spectrometer has been used with success for main elements determination on a limited number of ferroalloys. But this procedure has the disadvantage of being time consuming and labor intensive (ref. 7).

References

1. Gomez Coedo A., Jimenez Seco, J. and Lopez Rodriguez E. M., "Development of methodologies for instrumental analysis of ferroalloys", Progress of analytical chemistry in the iron and steel industry, Luxembourg, 1992
2. Bonvin D., Juchli K., "New developments in XRF", 6. Anwendertreffen Röntgenfluoreszenz- und Funkenemissionsspektometrie, Dortmund, 1999
3. Pétin J., Wagner A. and Bentz F., "Combination of oxidation and melt treatment for metal samples preparation for XRF analysis" Steel Research 56, 4, 1985
4. Giles H.L. and Holmes G.M., "The X-Ray fluorescence analysis of ferroniobium by a fusion method", X-Ray Spectrometry, vol. 7, 1978
5. Staats G., "Study of ferroalloys with the X-ray Fluorescence Analysis" Arch. Eisenhüttenwesen 45, nr. 10.
6. Rutherford R.T., "Ferroalloy Analysis by X-Ray Fluorescence Spectrometry" X-Ray Spectrometry, Vol. 24, 1993
7. Guerrero M.A. and Andres E., "New procedure of preparation and analysis of ferroalloys with additional advantages over current methods", Progress of analytical chemistry in the iron and steel industry, Luxembourg, 1996