

THE PREPARATION OF FERROCHROMIUM BY FUSED BEAD METHOD FOR XRF ANALYSIS

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BACKGROUND

Ferrochrome (FeCr) is an alloy of chromium and iron containing between 50% to 70% chromium by weight.

Ferrochrome is produced by electric arc furnace reduction of chromite. Most of the world's ferrochrome is produced in China, South Africa, Kazakhstan and India, which have large domestic chromite resources. Increasing amounts are coming from Russia. The production of steel is the largest consumer of ferro chrome, especially in the production of stainless steel with chromium content of 10% to 20% .

The particles in ferroalloys are very dense and a little porous, therefore the oxidation of the ferroalloy is a slower process than the oxidation of other samples, like oxides.

The preparation of Ferro-Chromium samples is more complex than for other ferro-alloys, because Chromium has a very low solubility in Borate fluxes. This constrains the analyst to working with small samples, of between 100 and 200 mgs.

The Ferro-Chromium samples are complicated to prepare due mainly to the existence of metallic Cr particles in its composition.

It is necessary to transform the non-oxidized metallic particles into oxides before carrying out the fusion of the sample otherwise there is a risk of seriously damaging the platinum crucible due to the alloying of the metallic chrome with the Platinum.

To transform the metallic elements into oxides, LiNO_3 and V_2O_5 are used as oxidizers.

The instrument used for the method is not a conventional muffle furnace, but a fusion machine manufactured by Navas Instruments. Due to the design of the Navas Quant Fusion machine there is no need to use 1200°C , as is common practice in the industry, but $1050^\circ\text{-}1080^\circ\text{C}$ to avoid flux evaporation that will occur above 1100°C and create an undesirable variable.

The machine used has a resistance furnace with very homogeneous temperature due to its circular design with capacity for up to 16 sample preparations per batch.

The method developed does not use crucibles and molds, as is standard in the industry but a single platinum-gold moldable that needs no pouring and leaves practically no residues in the moldable after fusion.

The moldables are not damaged by the ferro chrome oxidation and fusion and will only need some simple polishing after a lot of fusions have been performed.

It is necessary to prepare a bed of fused and cooled flux in the moldable to cradle the sample and oxidant, otherwise the platinum moldable will be exposed to unoxidized material and alloy with the metallic Cr, destroying the Pt moldable

The Quant Fusion instrument does all functions required automatically with no need to use an external muffle furnace: weighing of sample, flux and oxidants, flux bead preparation, first step

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oxidation, second step oxidation, agitation, cooling are all done automatically and programmed into the fusion unit controller

METHOD

1. The ferrochrome samples need to be prepared by reducing the particle size. This is achieved by grinding in a hardened steel grinding vessel to ensure that the average particle size is less than 80 mesh
 2. The furnace is set to 1000°C to prepare bed of fused flux in moldables
 3. The sample and oxidant are weighed into separate glass crucibles and the exact weights for the sample and the oxidants are recorded by the Navas Quant Fusion software.
 4. 5.5g of flux is weighed into each moldable.
 5. The system autoloader will load moldables into the furnace for about 10 minutes to fuse and create the protective flux bed, then come out with the assistance of the auto loader and be automatically cooled.
 6. During the 10 minutes of the pre-fuse cycle of the flux, the operator prepares the first step of oxidation.
 7. The sample and oxidant are intimately mixed and then transferred from the glass crucible to the fused flux bed in the moldable. It is evenly spread on the surface to maximize surface area for the oxidation process, which is a combination of the reaction with the LiNO_3 and the added air.
 8. A further 1.5 g of flux is added on the surface of the sample and oxidant and spread over the top of the sample to protect the crucible and moderate the oxidation reaction
- Fusion parameters**
9. Pre-oxidation temperature 580°C for 2 hours and 30 minutes with 5 liters of air flowing per minute, no agitation.
 10. The second oxidation is carried out by adding 0.500g of V_2O_5 added on ashless filter paper for quantitative transfer
 11. After the moldables have come out from the pre- oxidation first step and now in auto loader place all vanadium oxide bags one each in the moldables.
 12. The paper will burn and leave the vanadium oxide on top of the pre-fused sample oxidant flux mixture.
 13. The area should have a hood to take the possible gases from the burning of paper with vanadium oxide into a good extraction system.
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14. Final oxidation temperature of 1050° - 1070°C is held for 30 minutes, with agitation and mixing and an air flow of 5 liters per minute.
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15. Automatic drop of lithium bromide pellets 6-8 mg is done about 10 seconds before moldable extraction to assist with bead release.

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- a. The moldables are removed from the furnace automatically, after fusion and agitation to provide beads of excellent quality.

MEASUREMENTS

The resultant certified reference material beads were used to calibrate the Supermini 200 XRF spectrometer for Cr, Fe and Si and the unknown sample from Korea was characterized by reading the samples prepared in triplicate to show the repeatability of the preparation method measured against the calibrations. Empirical calibration model using theoretical alphas to correct for the influence of Cr and Fe on each other and automatically corrected using the Fusion Bead Correction protocol which accounts for the dilution and the chemical reaction of the LiNO_3 changing into Li_2O and the V_2O_5 changing into V_2O_3 , the oxygen being used to convert Cr to Cr_2O_3 and Fe to Fe_2O_3 .

RESULTS

Ferro Chrome Analysis

Sample ID	Cr, %	Cr %	Fe %	Fe %	Si %	Si %
NIST 64c -1	68.00	68.11	24.98	25.02	1.220	1.240
64c -2		67.89		24.99		1.275
64c -3		67.98		24.95		1.227
X		67.99		24.99		1.247
SD		0.11		0.04		0.025
RSD		0.16		0.14		1.990
NIST 196-1	70.84	70.71	28.5	28.34	0.371	0.380
196-2		70.91		28.48		0.406
196-3		70.81		28.62		0.430
X		70.81		28.48		0.405
SD		0.10		0.14		0.025
RSD		0.14		0.50		6.169
Korea 1		70.07		25.27		0.530
Korea 2		69.67		24.98		0.529
Korea 3		69.72		25.13		0.493
X		69.82		25.13		0.517
SD		0.22		0.15		0.021

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DISCUSSION OF RESULTS

The good correlation between certified values with measured values for the certified reference materials validates the method. The small spread between results for replicates is indicative of a repeatable sample preparation method that is well controlled. The complete oxidation can be visually checked by shining an LED source through the bead to ensure that there are no undissolved particles present.



Fig 1 – Incomplete Oxidation



Fig 2 – Complete dissolution and fusion

Resultant analysis shows the efficacy and repeatability of the method. All elements of interest including S and P can be quantified for complete characterization of Ferrochrome.

CONCLUSION

A robust, reproducible method for the preparation of ferrochrome in a borate fused bead to analyze the Cr, Fe, Si, S and P by direct XRF analysis and C determined by induction furnace analysis will allow complete elemental characterization for Ferrochrome to assist the steelmaker in accurate charge additions for the desired alloy recipe has been developed. Using the Navas Quant Fusion fused bead preparation instrument the two-step oxidation procedure is applicable to all ferrochrome samples and improves the ease of use over current methods of quantifying the elemental contents,

REFERENCES

1. R.T Rutherford, Ferro-Alloy Analysis by X-ray Fluorescence Spectrometry
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