Determination of Microamount of Carbon in Selected Samples of Iron, Steels, Ferro-Alloys and Metal Powder

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Summary: The influence of non-metallic components such as nitrogen, hydrogen and carbon has significant effect on the microstructure and ultimately on the mechanical properties of iron steels and ferro-alloy products. For the quantitative estimation of carbon content, some selected samples of iron, low alloy steel, high alloy steel, stainless steel, ferro-alloys, metal powders and the standards of these materials have been analyzed for the measurement of carbon content in microamount by using high frequency (HF) energy combustion and infrared (IR) detection technique. The accuracy of the method was evaluated statistically and the result data were compared with the literature values.

Introduction

Steels, iron and nonferrous metals are important structural materials mainly required for making of wires, sheets, railway lines, auto-mobile parts and all types of basic machinery. It is thus the fundamental industry from which many other industries are derived for the economic and industrial development of a country. All the industries paralyze if iron and steels industry is eliminated. The metal iron is a primary constituent of some of the most important engineering alloys. It is not easy to produce pure iron. However, it has been made with a total impurity content not exceeding 60 ppm, of which 10 ppm is accounted for by non-metallic impurities such as carbon, oxygen, sulphur and phosphorus, while 50 ppm represents the metallic impurities [1]. Carbon influences the physicochemical properties of iron, steels and nonferrous metals and commonly present from trace to percentage level in these materials. Pig iron, cast iron, steels, stainless steels and wrought iron differ in carbon contents and in presence of other alloying elements. The components of pig iron are approximately 4% carbon, 1.25% silicon, 1 to 2.5% manganese, 0.04% sulphur, 0.06 to 3% phosphorus and about 90% iron. Cast iron is essentially an iron-carbon (2-4%) alloy containing other elements such as silicon, manganese, sulphur and phosphorous, which modify the structure and properties of the resulting alloy markedly. White cast iron contains upto 2.5 - 4.0% carbon mostly as iron carbide (Fe_3C), this type of iron is very hard, brittle and unmachinable. On slow cooling due to partial graphitization of carbon it turns into malleable cast iron (2-3% carbon), ductile cast iron and gray cast iron (4% carbon). Wrought iron is a mixture of pure iron and silicate slag and carbon content is generally below 0.08%. Steels are alloys of iron and carbon in which the carbon content varies between 0.05% and 1.9%. In addition to carbon, steels contain minor amount of manganese, phosphorus, silicon, and sulphur, frequently it contains also aluminium. Carbon is the ruling element in steels. The strength and most other properties of steels depend on the size and distribution of carbide particles, that is, on the metallographic structure [2,3]. The stainless steel is an alloy steel, contains at least 12.5% chromium with some carbon content or a combination of 17.5% chromium and less than 7.5% nickel with different carbon content. The chromium-nickel stainless steels are very hard and most widely-used materials for the wear, corrosion, magnetic and heat resisting applications both at room and elevated temperatures [4].

The precise and accurate determination of non-metallic alloying elements especially carbon, is a permanent necessity in order to secure the product quality in foundries, in iron, steels and metal working industries. Different analytical techniques are available in literature for the determination of carbon content in metals and alloys i.e., the combustion of sample in arc discharge followed by

gas chromatography [5,6], neutron activation [7], combustion and nonaqueous photometric titration [8], modified wet chemical oxidation and nonaqueous coulometric titration [9,10], spark photometry [11], laser mass spectrometry [12], hydride formation and gas chromatography [13] and inductive heating in a stream of oxygen and determining the carbon dioxide (CO_2) by infrared absorption spectrometry [14-16]. The present work was carried out for the evaluation of accuracy, statistical reliability and economy of the technique for the measurement of carbon content in different samples of iron and stainless steels.

Results and Discussion

Calibration and optimization

Quantitative carbon determination was carried out by the absolute calibration technique. Calibration curve was plotted by means of the standard samples of steels with known contents of carbon. The points of standards were fitted exactly on the calibration curve using builtin computer programme inside the instrument. To find out the best conditions for analysis the automatic carbon analyzer CA 2001 was first calibrated and procedure of analysis was then optimized using the standard samples of steels. For this purposes different weights of standard samples were analyzed for weight optimization and results are presented in Table-1. The data indicates that the amount 0.5 gm was the optimum weight for the high to low carbon content. For optimization of the accelerator weight (tungsten granules), four standard samples were analyzed and results are shown in Table-2. The results data revealed that 1.5 gram of accelerator weight was optimum. Table-3 shows statistical analysis of standard samples of steel with variation in carbon content and different weights of the sample in order to get the percent deviation C.V., (Co-efficient of Variation), skewness, kurtosis and student's t-test values for the careful calibration of the instrument. The "Axum Scientific Graphic" and "TC-plot Statistical" Packages for personnel computer were used for all the statistical calculations. The t-test and skewness values of the standard samples emphasised the use of correct standard concentration and the accelerator weight for the accurate and precise analysis. The t-test values affirm the probability that whether the obtained result was highly significant or

Table-1: Carbon content of standard samples of carbon steels, low alloy steels and high alloy steels by varying sample weight for weight optimization

S.No.	Standard Samples	Sample Weight (gm)	Sample Contents (%)*	Reported values (%)[R]
1	BAM 228-1	0.5	2.050 ± 0.012	2.05 ± 0.002
	High alloy steels	1.0	2.004 ± 0.004	
		2.0	2.143 ± 0.113	
2	BCS 163/2	0.5	1.26 ± 0.011	1.26 ± 0.005
	Low Alloy Steels	1.0	1.17 ± 0.069	
		1.5	1.59 ± 0.043	
3	ECRM 030	0.5	0.456 ± 0.005	0.456 ± 0.004
	Low Alloy Steels	1.0	0.451 ± 0.004	
		1.5	0.458 ± 0.006	
4	ECRM 021-1	0.5	0.243 ± 0.002	0.248 ± 0.002
	Low Alloy Steels	1.0	0.239 ± 0.001	
		1.5	0.235 ± 0.004	
5	ECRM IRSID 281-1	0.5	0.048 ± 0.004	0.048 ± 0.002
	High Alloy Steels	1.0	0.047 ± 0.002	
		1.5	0.048 ± 0.001	

* = All values are represented as Mean ± Standard deviation.

Table-2: Carbon content of standard samples of carbon steels, low alloy steels and high alloy steels by varying accelerator (tungsten granules) weight for weight optimization.

S.No.	Standard Samples	Weight of Accelerator (gm)	Carbon Contents (%)*	Reported values Carbon Contents (%)[R]
1	BAM 228-1	1.0	2.004 ± 0.004	2.05 ± 0.002
	High alloy steels	1.5	2.05 ± 0.012	
		2.0	2.14 ± 0.113	
2	BCS 163/2	1.5	1.26 ± 0.011	1.26 ± 0.005
	Low Alloy Steels	3.0	1.19 ± 0.007	
3	ECRM 030	1.5	0.456 ± 0.005	0.456± 0.004
	Low Alloy Steels	3.0	0.441 ± 0.004	
4	ECRM IRSID 281-1	1.5	0.048 ± 0.004	0.048 ± 0.002
	High Alloy Steels	3.0	0.046 ± 0.001	

* = All values are represented as Mean ± Standard deviation.

not. The probability of significance of the results was compared with the true figures for the 10% and 5% tabulated values and the results are presented in Table-3. Results also indicated that weight should be increased for the low carbon content sample. On the basis of these results the optimal conditions were found i.e. the best sample weight was 0.5 gram and the accelerator weight was 1.5 gram. Using these optimum conditions, the selected samples of steels, stainless steels, ferro-alloys and metal powder were analyzed for determination of carbon contents and the results values are presented in Tables 4-6. All the data in Tables 4-6 represented the average of the four determinations. To assess the limit of detection and accuracy of the results, all the results data was statistically analysized. The standard deviation quoted refer to four measurements and Co-efficient of Variation (CV) was measured for each samples [17]. The limit of detection of carbon content for both steels and iron was found to be 0.05% ± 0.004 and 0.03% ± 0.001 respectively. The accuracy of limit detection results was found to be vary close as has been demonstrated already [18]. The limit of detection of carbon content means the limit given by

Table-3: Statistical analysis of standard samples of steels with high to low concentration for calibration of the instrument.

S.No.	Standard Sample	Sample Weigh (gm)	Carbon Contents (%)	Reported value Carbon Contents (%)	Percent deviation (CV)	Skewness	Kurtosis	Calculated t-test values
1	BAM 228-1	0.5	2.06 ± 0.008	2.05 ± 0.02	0.384	0.353	0.7994	4.86*
2	BAM 035-1	0.5	1.392 ± 0.023	1.31 ± 0.015	1.68	2.2097	0.6861	13.53*
3	BCS 163/2	0.5	1.139 ± 0.0205	1.26 ± 0.01	1.76	-2.095	0.638	-23.37***
4	ECRM 030-4	1.0	0.466 ± 0.025	0.456 ± 0.05	5.38	-1.458	0.717	1.48**

Co-efficient of variation (CV) = Standard deviation x 100/A. mean
Degree of freedom = 14
* High significant, **Significant, ***Not significant

the manufacturer in the instrument operating manual.

Table-4 portrays the results of per cent carbon content of various samples of iron (carbon steel). The results of carbon content measured by the inductive combustion technique were found to be similar with the literature values obtained by other different techniques [6-9]. The data of the Table-4 shows that the samples OC-23293, NC-23293, NE-167, G-3, and G-4 were high carbon steel and LCS-D, MSA-2892, MSB-2892, G-1, G-2, G-5 and S-1121 were medium carbon steel whereas rest of the samples were low-carbon steel. The sample NE-167 contained the highest level of carbon (0.817%) while the H-27494 have the lowest (0.053%). Some selected samples of ferro-alloys and tungsten metal powder were analysed for the carbon contents and their results are also presented in Table-4. The influence of carbon on the mechanical and physical properties of iron and ferro-alloys are of considerable interest in the past. Steels and iron are important because both represent by far the most widely-used metallic materials, primarily due to the fact that they can be manufactured relatively cheaply in large quantities to very precise specifications. Steels and iron comprise well over 80% by weight of the alloys in general industrial use. Steels form perhaps the most important group of alloys in common use. Therefore, in studying them it is useful to consider the behaviour of pure iron first, then iron-carbon alloys and finally examine the many complexities which arise when further alloying addition are made. The addition of carbon to iron is sufficient to form a steel. However, steel is a generic term which covers a very large range of complex composition. The presence of even a small concentration of carbon, e.g., 0.1 - 0.2% weight percent, has a great

Table-4: Carbon Contents of Iron (carbon-steel), Ferro-Alloys and Metal Powder.

S.No.	Sample Description	Samples Identification	Carbon Content (%)*	Certified Values[a] (%)
1.	Iron (Carbon Steel)			
		MS-1	0.292 ± 0.034	0.28
		M.S-2	0.196 ± 0.029	0.20
		M.S-A	0.179 ± 0.006	0.18
		M.S-B	0.179 ± 0.008	0.18
		LCS-D	0.329 ± 0.007	0.32
		MSA-2892	0.372 ± 0.008	0.38
		MSB-2892	0.404 ± 0.002	0.38
		MSA-7992	0.208 ± 0.004	0.39
		OC-23293	0.200 ± 0.003	0.192
		NC-23293	0.527 ± 0.044	0.52
		A-28493	0.226 ± 0.007	0.22
		B-28493	0.226 ± 0.008	0.23
		C-28943	0.185 ± 0.010	0.19
		NE-167	0.817 ± 0.008	0.80
		G-1	0.489 ± 0.007	0.50
		G-2	0.470 ± 0.010	0.48
		G-3	0.523 ± 0.03	0.52
		G-4	0.526 ± 0.003	0.52
		G-5	0.426± 0.010	0.42
2.	Ferro-Alloys			
		A-27494	0.217 ± 0.002	0.23
		B-27494	0.104 ± 0.011	0.10
		C-27494	0.146 ± 0.001	0.15
		D-27494	0.134 ± 0.004	0.13
		E-27494	0.210 ± 0.003	0.23
		F-27494	0.203 ± 0.002	0.20
		G-27494	0.074 ± 0.006	0.07
		H-27494	0.053 ± 0.003	0.06
		I-27494	0.087 ± 0.001	0.09
		S-1121	0.435 ± 0.060	0.42
		FN-2811	0.278 ± 0.007	0.28
3.	Tungten metal powder	WI-S	0.03 ± 0.005	0.03
		WL-1	0.005 ± 0.007	0.005
		WL-2	0.007 ± 0.002	0.007

[a] Metals hand books, 2nd. Ed. Edited by J.R. Davis, Davis Associate, ASM International Materials Park, OH 44073-0002, U.S.A. 1998.
[b] Smithells Metals Reference Book, 6th edition Ed. Erica Brandes, Butterworth & Co. Ltd. London, 1983
*= All values are represented as Mean ± Standard deviation.

strengthening effect on iron. Steels may be classified by the broad range of carbon content such as, low-carbon steel; upto 0.25% carbon, medium carbon steel; 0.25 to 0.55% carbon and high carbon steel; above 0.55% carbon [19]. It has been observed by Coates and Leyshon [20] that hardness of steels and iron increases as the carbon content increased and upto about 0.85% carbon the effect on hardness is marked while above 0.85% carbon, the hardness

increases very slowly. The NE-167 is a hard iron sample due to high carbon content i.e., 0.817%. The ferroniobium sample FN-2811 contained 0.28% ± 0.007 carbon. The sufficient amount of niobium is added to the steel to combine with all the carbon for the precipitation of niobium carbid [19, 20].

The data of Table 5 revealed percent carbon contents in various cast iron samples and the amounts detected were between 1.156 - 3.81% ± 0.03. Sample of cast iron V-29695K contained the highest carbon than the CSNB-146. Cast iron like steels are basically alloys of iron and carbon. Many cast irons contain between 2 and 6.67 percent carbon. Since high carbon content tends to make the cast iron very brittle and carbon contents of most commercial irons fall between 2.5 and 4.0 percent. Carbon can be combined as iron carbide in cementite or it can exist as free carbon in graphite. The shape and distribution of the free carbon particles greatly influence the physical properties of the cast iron. The high carbon content iron, when commercially produced, are known as white or cilled irons and are hard, brittle and unmachinable. The results of carbon contents in different samples of stainless steels are presented in Table 6. The carbon contents of SS 308L rod samples were found to be similar with the chemical and high temperature corrosion resistance 308 series stainless steels [18]. The samples SS 304-1 and SS 304-2, contained 0.121% carbon and these values are very close to the high resistance to pitting during welding 304 austenitic stainless steels series. Carbon content in steels chips and low alloyed steels were found in the range of 0.092 - 0.298% ± 0.013 [19, 20].

Experimental

Selected samples of steels, stainless steels, ferro-alloys were obtained from Alloy Development Group, NMD, PINSTECH. Automatic Carbon Analyzer (LEYBOLD-HERAEUS C A 2001) was used for the determination of carbon contents. The whole system consists of electronic control module, high frequency (HF) inductive combustion furnace and gas conditioning system with infrared unit as shown in Figure 1. The instrument was calibrated with standard samples containing about 2% carbon to ascertain the precision and accuracy of the method.

Table-5: Carbon Contents of Cast Iron

S.No.	Sample Description	Samples Identification	Carbon Content (%)*	Certified Values[R] (%)
1.	Cast Iron			
		CS-20593	2.658 ± 0.005	2.65
		CSNB-146A	1.156 ± 0.204	1.15
		CSNB-146B	2.026 ± 0.376	2.05
		DPLC	3.58 ± 0.057	3.60
		V-29695K	3.81 ± 0.056	3.80
		B-29695K	3.75 ± 0.056	3.80
		T-I-K	3.55 ± 0.035	3.60
		CINC	3.46 ± 0.201	3.45
2.	Bearing Housing Plate	GS-ISX	3.58 ± 0.3	3.60
3.	Cast Iron Turnings	CINCT	3.28 ± 0.04	3.30

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® Smithells Metals Reference Book, 6th edition Ed. Erica Brandes, Butterworth & Co. Ltd. London, 1983
*= All values are represented as Mean ± Standard deviation.

Table-6: Carbon Contents of Stainless Steels

S.No.	Sample Description	Samples Identification	Carbon Content (%)*	Certified Values[R] (%)
1.	S.S. 308L rod	308-B	0.050 ± 0.004	0.03
		308-M	0.04 ± 0.0004	0.08
		308-S	0.073 ± 0.0087	0.03
2	Steel Electrode	ELD	0.100 ± 0.014	0.10
		EMD	0.145 ± 0.018	0.15
		ESD	0.205 ± 0.018	0.20
		SSW	0.052 ± 0.004	0.05
3	S.S-304	SS-304-1	0.121 ± 0.009	0.08
		SS-304-2	0.121 ± 0.007	0.08
		A-216	0.309 ± 0.005	0.32
4	Steels Chips	SC-12892	0.068 ± 0.007	0.07
		S-27593	0.298 ± 0.003	0.28-0.33
		WS-1	0.182 ± 0.095	0.18
		WS-2	0.167 ± 0.061	0.17
		SS-25/6A	0.092 ± 0.007	0.10
		SS-25/7A	0.123 ± 0.011	0.12
		SS-25/9A	0.185± 0.006	0.18
5	Low alloy steels	S-296	0.135 ± 0.014	0.13
		HS-1	0.257 ± 0.015	0.25
		HS-2	0.173 ± 0.047	0.18
		HS-3	0.171 ± 0.032	0.17
		POL-1	0.212 ± 0.01	0.22

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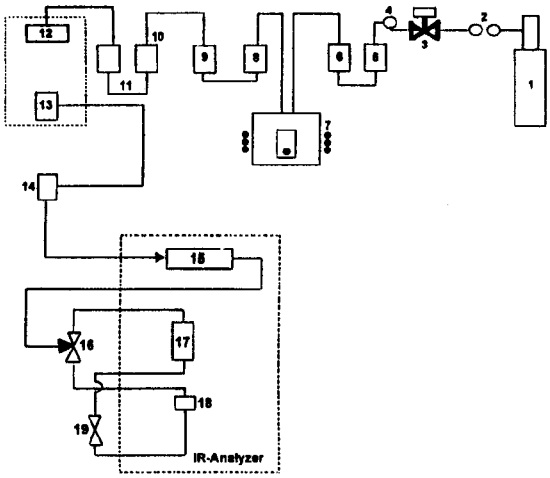
® Smithells Metals Reference Book, 6th edition Ed. Erica Brandes, Butterworth & Co. Ltd. London, 1983
*= All values are represented as Mean ± Standard deviations.

Sampling

Different sampling techniques were used in accordance with ASTM specifications [21], for different categories of samples of stainless steels and ferro-alloys. Uniform chips sample in ~ 1.18 mm dimensions made free of grease, dirt and dust were used. The sheet specimens about 50 mm in width were cut across the full width, cleaned by pickling or grinding and then folded the ends together. Samples were taken by milling from the middle of this length.

Procedure

The experimental approach used in this study was based on the standard ASTM specification [17], single sample per crucible technique for the quantitative determination of carbon content in iron



1. Oxygen Cylinder
2. Pressure Reducing Valve
3. Solenoid Valve
4. Pressure Guage
5. Water Trap
6. Carbon dioxide Trap
7. HF Combustion Furnace
8. Dust Trap
9. Water Trap
10. Catalyzing Oven
11. Sulphur trioxide Trap
12. Flow Controller
13. Carbon dioxide Test Cell
14. Flow Indicator
15. Flow Control
16. Three Way Valve
17. Cell
18. Change-over Valve
19. Change over Valve

Fig. 1: Gas Conditioning System and IR - Unit for Carbon Analyzer

and steels. A blank test was carried out for necessary correction because the disposable ceramic crucible and added tungsten granules used as an accelerator material produce small amount of carbon. Crucible along with accelerator material was analyzed to get the blank values. Approximately 0.5 gm sample in the form of chips or powder was weighed in ceramic crucible and melted in impulse furnace at specified temperature higher than melting point. Sample was heated upto and was oxidized in a high frequency energy combustion furnace. The oxidation products of the combustion process i.e., H_2O and CO_2 were cleaned after passing through a dust trap and the water vapours were removed by the water absorption trap. The sulphur content of the sample was converted into SO_2 which by a catalytic re-oxidation was changed into SO_3 and absorbed in sulphur trioxide absorption trap. The residual CO_2 and the carrier gas oxygen was led to IR cell. The resulted analogue signal produced by IR analyzer was amplified and integrated which provides a unique measure of quantity of carbon content (as carbon dioxide) of sample.

Conclusion

High frequency inductive combustion technique for the estimation of carbon contents in metals, mainly consists of heating of the sample in high frequency energy, combustion in oxygen, and analysis of the combustion products in the infrared analyzer, possesses several advantages over the other techniques such as spectrometry, coulometry and conductivity measurement. It is more versatile, easy operation system, swift, less time consuming and in general more economical. Its results are more accurate and statistically reliable. This method of analysis can be applied perfectly in routine sample analysis during production processes, from the raw material upto the final product, as well as to the quality control.

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