

CHEMICAL ANALYSIS OF SELECTED CARBON STEEL ARTEFACTS FROM BENIN CITY AND IMPLICATIONS FOR PRESERVATION

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ABSTRACT

The use of carbon steel in the fabrication of outdoor artefacts is widespread in Nigeria. The peculiar morphology of this material makes it susceptible to atmospheric corrosion, which ultimately can weaken and destroy carbon steel artefacts and consequently their embodied aesthetic and historic values. Using Benin City, taken to be representational of other metal artefacts fabrication contexts in Nigeria as case study, this study investigated the elemental composition of some carbon steels used in the fabrication of outdoor artefacts with a view to determining finishing options for the material to withstand corrosion. Three Ion Beam Accelerator techniques: Particle-Induced X-Ray Emission Spectroscopy, Rutherford Backscattering Spectrometry and Proton Induced Gamma-Ray Emission Spectroscopy were used simultaneously to determine the elemental composition of twenty three sampled items. Optical Emission Spectrometry was also used in determining the carbon content in the items sampled. Ten elements: C, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, and Zn were detected and measured. The carbon steels compositions, when compared with global standards, were found to be deficient. This raised issues on how such materials can withstand corrosion and corollary to which the study recommended the need for Nigeria to set standards for the quality of steel produced in the country and those imported into Nigeria. Significantly, the study also recommended a two-way coating, among other finishing options, to protect outdoor carbon steel artefacts from atmospheric corrosion and that, where one cannot get good quality standard carbon steels, an in-depth knowledge of preservation techniques becomes imperative.

Keywords: Carbon steel; elemental composition; preservation of artefacts; outdoor artefacts in Nigeria; ion beam accelerator techniques; optical emission spectrometry

1.0 INTRODUCTION

Metal is a familiar material used in diverse applications. There are two main groups of metals. These are ferrous and non-ferrous metals. Iron and its alloys are grouped as ferrous metals with steel as an important alloy of iron. Buttressing this argument, Seblin, Jahazeeah, Sujeebun, Mahohar and Wong (2012) argued that steel is a term used for many different alloys which vary in both the way they made and in the proportions of the materials added to iron. Specifically, carbon steel, the metal under study, is an important type of commercial steel alloy. Other types of commercial steels are low-alloy steels and high-alloy steels (Capudean, 2003).

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Generally, in the alloying of steel, small amounts of other elements are added to give it special qualities that allow it to be employed in a variety of applications. These elements include manganese, carbon, copper, chromium, nickel, vanadium, molybdenum, aluminium, boron, titanium, calcium, nitrogen and tungsten (Seblin et al., 2012). In the case of carbon steel, each alloying element has its specific effect. Some of these effects include durability, ductility, corrosion resistance, toughness and hardenability. What is implicit here is that basically all metal types are susceptible to one or more forms of corrosion, even though some are more susceptible to same type of corrosion than others. Specifically, ferrous metals are more susceptible to atmospheric corrosion than non-ferrous metals. This underscores the notion that metals are durable and capable of surviving for centuries, unaffected by atmospheric conditions. Despite the effects of some of the alloying elements however, the peculiar morphology of carbon steels makes them susceptible to atmospheric corrosion. In other words, carbon steels suffer weathering as a result of exposure to atmospheric condition. This can ultimately weaken and destroy carbon steel artefacts alongside its embodied symbolic, historic, and aesthetic value.

Carbon steels in the forms of sheets, rods, sections and bars are used in engineering, and in the fabrication of artefacts ranging from jewellery pieces, sculptural pieces to outdoor gates railings, decorative and furniture pieces. Basically, in the production of steels, there are standards. It is in this regard that some countries and organizations have set standards for steel production. Indian, Britain and Mauritania are some notable countries with known standards for steels. Also, according to Seblin et al., (2012), American Society for Testing and Materials (ASTM), American Iron and Steel Institute (AISI), Society of Automotive Engineers (SAE), International Standards Organization (ISO) and National Bureau of Standards are some outfits that set standards for steels and other products. These Organizations also ensure that the produced carbon steels are in conformity with set standards.

In Nigeria, especially Benin City, the use of metals for articles' fabrication is not new. The ancient city is globally renowned for her copper alloy castings and iron (steel) artefacts. Igbinokpogie, Lawal, and Ekhaton (1997); Andah (1982); Connah (1975) have variously noted the iron working capabilities of Benin metal workers, especially in the fabrication of tools, weapons and figures. The Benin metal workers have also attempted conservation of iron artefacts produced. In a study of Benin curatorial practice, Eghafona and Okpoko (2004) noted that metal workers in Benin City saw the need to care and preserve cultural materials produced.

Following the trend of developments in metal arts of Benin, the use of steel in the fabrication of artefacts also enjoyed patronage. Welded steel gates were designed and produced to meet the aesthetic and functional demands of buildings and construction. However, underlying the aesthetic and functional import of these carbon steel artefacts are challenges of their preservation. Essentially, the preservation of an artefact refers to all the means and actions aimed at avoiding and minimizing deterioration or loss of parts or the whole artefact. The preservation of an artefact starts with the finishing of the artefact. It is also of crucial importance that knowledge of the material composition of any material is essential in preservation options for the said material. As Janssens, Vittiglio, Deraedt, Aerts, Vekemans, Vincze and Snigirev (2000) aptly put it, scientific analysis of artefacts is important in deciding how best to preserve, conserve and restore artefacts. Such analysis is centred on the elemental composition of the artefacts.

The study of carbon steels in Nigeria is not quite new. However, most of the studies are basically engineering-based as they dealt specifically with the tensile strength of steel bars used in building. For instance, Jibrin and Egeh (2013); Kareem (2009); Alabi and Oyeji (2010); Arum (2008), investigated the chemical compositions of reinforcing steel bars used in the construction of buildings. Similarly, Fadare, Fadare and Akanbi (2011) studied the effect of heat treatment on mechanical properties and microstructure of steel. Studies on the qualitative and quantitative nature of carbon steels used in production of artefacts are obviously missing. It is against this background that this analytical investigation of the qualitative and quantitative elemental composition of a wide range of carbon steels used particularly in the fabrication of artefacts was conducted. The study used Benin City as the case study; as the city is taken to be presumptuous of other metal artefacts production contexts in Nigeria.

The items studied are plain carbon steel rods, strips, wires and sheets commonly used in the fabrication of gates, railings and other sculptural pieces. It is imperative to mention here that field investigation revealed that the metal artists in Benin City who work with carbon steel have some knowledge of and the need to preserve artefacts. Most carbon steel artefacts were consequently coated with glossy paints as their finishes for preservation and aesthetic qualities.

For the experimental investigation, two different materials study protocols were used. These are Ion Beam Accelerator (IBA) based techniques and Optical Emission Spectrometry (OES). The result of the characterization of the steel items was compared with global standards of carbon steels following which suggestions for better preservation strategies were drawn. Such data, it is hoped will be of use generally to engineers and especially craftsmen and artists who employ carbon steels to produce art objects and artefacts. Owners of such artefacts and curators of carbon steel artefacts will similarly benefit from findings of this study.

2.0 MATERIALS AND METHODS

2.1 Samples Collection and Preparation

A total of twenty-three (23) carbon steel items studied were collected between 2012 and 2015 from Benin City. Where possible, the samples were directly taken from artefacts. Others were collected from architectural steel workers who employ various forms of carbon steels in the fabrication of artefacts. The sampled items consisted of three (3) strips (also called flat bar), six (6) rods, seven (7) pipes, three (3) angle bars and four (4) sheets. From each of the items, a small fragment measuring about 1 cm square was cut off. The size of the fragments was predetermined to fit the sample holder of the IBA. The fragments were abraded with 80C grade of emery paper to remove all forms of rust.

The twenty-three sampled items (Figures 1 - 23) were grouped by their forms and tagged with pseudo names accordingly. The carbon steel strips samples were coded CBS STRP; the rods, CBS RD; pipes, CBS PP; angle bars CBS AB and CBS SHT representing sheet.



Figure 1. CBS STRP1



Figure 2. CBS STRP2



Figure 3. CBS STRP3



Figure 4. CBS RD4



Figure 5: CBS RD5



Figure 6. CBS RD6



Figure 7. CBS RD7



Figure 8. CBS RD8



Figure 9. CBS RD9



Figure 10. CBS PP10



Figure 11: CBS PP11



Figure 12. CBS PP12



Figure 13. CBS PP13



Figure 14. CBS PP14



Figure 15. CBS PP15



Figure 16. CBS PP16



Figure 17. CBS AB19



Figure 18. CBS AB18



Figure 19. CBS AB19



Figure 20. CBS SHT20



Figure 21. CBS SHT21



Figure 22. CBS SHT22



Figure 23. CBS SHT23

2.2 Analysis

The elemental analysis of the sampled items was done using a combination of three complementary IBA based techniques of PIXE, RBS, and PIGE as well as OES. The application of two or more materials analysis protocols for elemental analysis is commonplace in materials science. Specifically, the use of two or more analysis protocols in the study of steel samples is aimed at obtaining very good overall result of elemental composition (Ene, Popescu, Babica & Besliu, 2006). For the carbon analysis of the items sampled, Optical Emission Spectrometry (OES) facility at National Metallurgical Development Centre (NMDC), Jos, Nigeria was employed. The Ion Beam Accelerator used in this study is situated in the Tandem Accelerator Laboratory of the Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife, Nigeria. The Tandem Accelerator is centred around a NEC 5SH 1.7 MV Pelletron Accelerator equipped with RF charge exchange ion source. The ion source is equipped to provide proton and helium ions. The end station is made up of an aluminium chamber of about 150 cm in diameter and 180 cm height. It also houses four ports and window; port 1 at 165° is for the RBS detector, port 2 at 135° is for PIXE detector, port 3 at 30° is for ERDA detector, the window at 0° is for observing the beam position and size, while port 4 at 270° is for PIGE detector. An appropriate pinhole filter also called funny filter that has a 20% hole at the centre was placed in front of the Si (Li) detector. The filter which is an X-ray absorber was useful in the study of thick samples as well as the simultaneous analysis of both light and heavy elements in the target samples. The X-ray spectra from the PIXE measurements were analyzed with computer-coded GUPIXWIN software. To ensure the accuracy of the experimental procedures, an in house calibration of the Ion Beam Accelerator and OES Spectrometer were performed using the Standard Reference Materials (SRM) and the National Institute of Standards and Technology (NIST SRM) 1139a, 1761a and Nigeria Industrial Standard (NIS) 1992.

The choice of the IBA based techniques of PIXE, RBS and PIGE and OES is hinged on their suitability to the items under study. Essentially, these three IBA techniques produce both qualitative and quantitative analysis. They are also non-invasive, non-destructive and allow depth profiling of samples. Fazinic et al. (2010) have also noted these techniques are renowned for accuracy of the information obtained). In the opinion of Lahanier, Amsel, Heitz, Menu and Anderson (1986), any scientific technique for analysing valuable art and cultural objects should be “non-destructive, fast, universal, versatile, sensitive and multi-elemental”. Similarly, OES offers rapid elemental analysis of solid metal samples making it indispensable for quality control (Schimadzu, 2016).

3.0 RESULTS AND DISCUSSION

A summary of the results of the elemental analysis of the twenty-three (23) carbon steel items sampled are expressed in the Table 1. The values of carbon ranged from 0.16% to 0.42% thus placing the sampled items in two categories of carbon steel. These are low carbon steel also called mild steel and medium carbon steel. In carbon steel classification by Untracht (1975), mild steel or low carbon steel, contains between 0.15 – 0.30% of carbon, medium carbon steel, 0.30 – 0.50% of carbon and high carbon steel, 0.50 – 1.60% of carbon. What can be deduced from this classification with regards to the elemental composition of all the twenty-three items sampled is that CBS STRP2, CBS STRP3, CBS RD4, CBS RD9, CBS PP11 and CBS PP13 fall in the range of medium carbon steels. In this same regard, the other items are low carbon steels.

Table 1: Summary of elemental composition of twenty-three (23) carbon steel items sampled.

Item/ (%). Code.	Calculated elemental composition in weight percentage								
	<i>C</i>	<i>K</i>	<i>Ca</i>	<i>Ti</i>	<i>Cr</i>	<i>Mn</i>	<i>Fe</i>	<i>Ni</i>	<i>Cu</i>
Zn									
CBS STRP1	0.28		0.06		0.09	0.67	96.2	0.18	0.91
CBS STRP2	0.38		0.29		0.13	0.71	97.4		
CBS STRP3	0.42		0.27	0.06		0.63	98		
CBS RD4	0.31				0.20	0.87	98.2	0.19	0.29
CBS RD5	0.28	0.28	1.2	0.25		0.40	96.6		0.11
CBS RD6	0.18		0.07		0.16	0.65	98	0.12	0.29
CBS RD7	0.30					0.83	98.6		0.14
CBS RD8	0.26				0.09	0.36	99		0.16
CBS RD9	0.32			0.06	0.11	0.19	99		0.09
CBS PP10	0.09		0.16	0.06		0.19	99		
CBS PP11	0.32			0.06		0.78	98.8		
CBS PP12	0.26		0.07	0.08	0.30	0.16	98.5	0.12	0.08
CBS PP13	0.25					0.31	99.1		
CBS PP14	0.26			0.06		0.19	99.4		
CBS PP15	0.26		0.10	0.06		0.19	99		
CBS PP16	0.18			0.06	0.07		99.1		
CBS AB17	0.28					0.63	97.3		0.07
CBS AB18	0.28		0.18			0.56	98.8		
CBS AB19	0.16					0.19	99.1		
CBS SHT20	0.09		0.16	0.06			99		
CBS SHT21	0.09		0.23	0.07	0.04		99		
CBS SHT22	0.08					0.30	99.3		
CBS SHT23	0.22					0.17	99.6		

Low carbon steels, in the classifications by Cardarelli (2008); Timken (2011), range from AISI – SAE grades 1000 – 1030, with their chemical composition range as; carbon (C) .06% – .28%, manganese (Mn) .25% – .60%, phosphorus (P) maximum .040%, sulphur (S) maximum .050%; balance, iron (Fe) and other trace elements. In the case of medium carbon steels, they range from AISI – SAE grades 1030 – 1055. Their chemical composition range is; carbon (C) .28%/.34% – .050%/.60%, manganese (Mn) .60% – .90%, phosphorus (P) maximum .040%, sulphur (S) maximum .050%; balance, iron (Fe) and other trace elements (Cardarelli, 2008; Timken, 2011).

Findings from the analysis further revealed that while the percentage of iron in all the twenty-three items sampled is in agreement with global standards, same cannot be said of the manganese, phosphorus and sulphur. Manganese was not detected in items CBS PP16, CBS SHT20 and CBS SHT21. Even when the value of manganese in items CBS RD9, CBS PP10, CBS PP12, CBS PP13, CBS PP14, CBS PP15, CBS AB17, CBS AB19, CBS SHT22 and CBS SHT23 was compared against AISI and SAE standards of low carbon steel and medium carbon steel, it fell short. Phosphorus and sulphur were also not detected in any of the items tested. There were some other elements that were detected in low values and as trace elements in some of the items studied. For instance in CBS RD5 Ca was detected with a value of 1.2% and K_a, detected and measured with

a trace value of 0.28%. Ca was also detected and measured as trace elements in ten (10) items in the range of 0.06% – 0.29%. Similarly, in eleven (11) items, Ti was detected and measured in the range of 0.06% – 0.25%. Some other items had traces of other elements. These are Cr which was detected and measured in nine (9) items in the range of 0.04% - 0.20%, Ni, in four (4) items in the range of 0.12% - 0.19%, Cu, in nine (9) items in the range of 0.07% - 0.91%, while Zn, was detected and measured only in CBS RD7 with a trace value of 0.06%.

Although some of the above alloying elements are of low values and some others, traces, they are however beneficial to carbon steel. For instance Mn and Ti, that were measured in trace values in some of the items sampled have been identified by Seblin et al. (2012) as contributing greatly to increased strength and hardness in carbon steel. Similarly, Copper in trace value renders the carbon steel more resistant to corrosion. But in higher values, copper could be harmful to the carbon steels surface quality (Seblin et al., 2012). Phosphorous, which was not recorded in any of the items studied, is classified in AISI and SAE standards. Phosphorous is a significant element in carbon steel as it helps to improve the corrosion resistance of weathering steels (Totten, 2007; Reardon, 2011; Schweltzer, 2010; Gupta, 2010: 64). Specifically, Schweltzer (2010) noted that an increment of phosphorous from less than 0.01% to 0.1% leads to between 20% – 30% improvement in the corrosion resistance of copper-bearing carbon steels; this is occasioned by P forming layers of insoluble phosphates which acts as barriers to corrosion in steels. Sulphur with values stated in AISI and SAE standards was also not detected in any of the items sampled. While it is argued that increased value of sulphur in carbon steel may be negative, sulphur in a range of 0.08% - 0.33% is intentionally added to carbon steel to improve its fatigue life.

What can be deduced in all of the foregoing elemental analysis is that the carbon steel items sampled are not quite in conformity with global standards. For instance, phosphorous, an element that helps carbon steel resists atmospheric corrosion was not detected in any of the items sampled. Copper, another element that helps carbon steel in resisting atmospheric corrosion was detected in only nine (9) out of the twenty-three (23) items sampled. All of these have implication for artefacts fabricated from these carbon steels, especially those that are exposed to atmospheric conditions, which would normally necessarily require planned preservation intervention for their longevity. In essence, the carbon steel items sampled are disadvantaged by the absence of corrosion resisting elements. The resultant effect leaves artefacts made of the sampled items more susceptible to atmospheric corrosion especially when not well preserved.

4.0 CONCLUSION AND RECOMMENDATIONS

The absence of crucial elements, such as phosphorous and copper, in carbon steel raises issues on how such materials stand the test of corrosion. Corollary to this is the fact that any artefact made of such material would be highly susceptible to corrosion. And if the artefact is to be cited outdoors, it will suffer greater pressure of atmospheric conditions; thus, irrespective of the preservation intervention, especially when such intervention is not deliberate, corrosion will quickly set in, and the artefact will deteriorate.

Against the foregoing background, there is the urgent need for Nigeria to set standards with regards to the quality of steel produced in Nigeria and those imported into the country. Quality control organizations like the Standard Organization of Nigeria (SON)

should put in place an effective system to monitor the quality of carbon steel forms produced in Nigeria as well as those imported.

On preservation of artefacts made of carbon steel, it is important for metal smiths and artists in Benin City and elsewhere in Nigeria to be well informed of global trends in finishing outdoor carbon steel artefacts. As Mandeno (2008) suggests, it is important to remove all salts, rusts and iron scales from the surface of carbon steels before coating. If these are not done, it could result in blistering and eventual rupture of the coating. There are quite a number of options in protecting carbon steel artefacts from atmospheric corrosion; the two-way coating option however remains the best and most cost effective method to protect outdoor carbon steel artefacts from atmospheric corrosion (Kaplan, 2010; Mandeno, 2008; Dulux, 2009). In this two-way coating option, primers and top coats are used. Specifically, high performance vinyl or epoxies are used as primers while polyurethane paint is used for top coat. Further to this, regular inspection of the carbon steel artefact for coat failure remains significant in planned preservation scheme. Indeed the local craftsman really has no business engaging in scientific analysis of materials. His is to purchase the metals he employs in artefacts fabrication. It is taken for granted that the metals procured are intact. However, where one cannot get precise and good quality of standard carbon steels, the option of an in-depth knowledge of preservation becomes imperative.

ACKNOWLEDGEMENT

The authors would like to express our appreciation to University of Benin and Ladoko Akintola University of Technology for support throughout the research project.

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