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SURFACE PATINA AND CLAY CHARACTERIZATION: MULTI-ANALYTICAL INVESTIGATIONS INTO *BIDRI* HANDICRAFT

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Abstract

Bidri handicraft in India, patronised by Bahamani kings, dates back to the fifteenth century and is nowadays under operational and socio-economic threats. The craft is made of zinc alloy, which poses scientific challenges in the areas of metallurgy, metal oxidation, and surface science. In the present paper, the art, owing to its scientific enigma, is under scrutiny, wherein the handicraft mandates the use of Bidar Fort (in Karnataka, India) clay, which bestows the handicraft its characteristic matt-black patina. The fort is a heritage conservation site and thus poses a threat to the perennial practice of handicraft. Therefore, it is imperative to document the patina and fort clay. Thus, morphological and chemical characterization of Bidri artefact surfaces was accomplished using scanning electron microscopy (SEM), X-ray Diffraction (XRD) analysis, X-ray Photoelectron Spectroscopy (XPS), and Energy Dispersive X-ray fluorescence spectroscopy (ED-XRF); besides, elemental characterization of Bidar fort clay was accomplished using SEM coupled with energy dispersive X-ray spectroscopy (EDS). This study is significant, as it is one of the initial works to scientifically document Bidri handicraft surface and clay, besides laying the foundation for future studies; a step to conserve the handicraft; and a step to prevent the deterioration of the Bidar fort monument.

***Keywords**: Surface patina; Clay characterization; Bidri Handicraft; Bidar fort; Zinc-copper alloy; Clay oxidative properties*

Introduction

India is one of the ancient seats of practicing metal-art [1], and one such ancient metalcraft has been the *Bidri* handicraft [2]. The availability of metal mines, foundries, and dexterity with metallurgical knowledge was one of the primary reasons for metalcrafts to flourish in the country. This dexterity with metal encouraged craftsmen of the times to cater to the royalty by producing artefacts of aesthetic utility, like the *huqqas* (hubble-bubble), ornament boxes, pitchers, figurines, and other articles [3]. India is attributed to be the birthplace of zinc metal dating back to the 5th century BCE, supported by the excavations found in Lothal and Atranjikhera, in the Indian states of Gujarat and Uttar Pradesh [4, 5]. Another narrative that supports this claim is the presence of mining ores in Rajasthan, right from the Bronze age, i.e., from the mid-fourth millennium BCE [6, 7]. Further, as bronze is a copper alloy with zinc (and tin), it is obvious that zinc ores must have been prevalent before the bronze age.

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The past few decades have witnessed few studies on the Bidri handicraft, with a specific focus on its metallurgical excellence [8, 9], though many of these have been inconclusive. This gives sufficient evidence for studying the handicraft from diverse dimensions, perspectives, and knowledge. The manuscript characterises the surface-patina of the *Bidri* handicraft and primary soil analysis, which could be a humble step towards partially shedding the enigmas around the craft, besides offering rudimentary clues for future investigations. Diligent research could be commissioned, as complementary research can establish insights on the development of metallurgical knowledge and scientific know-how in the 15th century A.D., to which the origins of this craft are attributed.

Bidri Handicraft

One of the earliest accounts of *Bidri*-handicraft is witnessed in the works of Sir Benjamin Heynes, while mentioning *Bidri* as *Biddery (vidri)* [10]. Bidri-ware is a class of inlay damascening [11] known as *koftagiri*, made in silver [12], with a characteristic black patina.

The handicraft dates to the 15th century, the Bahamani era, in the state of Karnataka, India. The town of Bidar is where the handicraft gets its name: *Bidri* (Fig. 1), the erstwhile capital of the Bahmani sultans, under whose patronage the craft migrated to India, was widely recognised, and gained prosperity.

Fig. 1. Bidar Fort (prime premises) and core premises from where Bidri clay is quarried for surface patination of handicrafts

The handicraft is a class of Islamic metallurgical perspicacity, evidence of which is prominent in the seventeenth century, though substantial support has been accrued for its practice since the 15th century A.D. [13, 14]. The handicraft is reported to be zinc alloy with a characteristic jet-black matte finish, as represented in Fig. 2, decorated with non-ferrous metals like silver, gold, and rarely copper engraving [15].

It is made of an alloy with amalgamation of zinc and copper, when traditionally treated with Bidar fort clay (Fig. 2), develops a jet-black protective layer i.e., patina, identified as zinc oxide and hydroxide which diminishes the rate at which any further corrosion of the surface can occur [16]. The anti-corrosive capabilities have been tested with a plethora of applications, when *Bidri* products are used for storing water, betel-leaf etc., and also tested with heat, (exposure to) atmosphere or human-touch. A lot of this anti-corrosive characteristics has been attributed to the black patina that is formed. The characteristic is accredited to the presence of copper in the alloy; as technically, none of the zinc compounds are black in colour. Thus, the patina of *Bidri* handicraft has been a subject of metallurgical enigma, equally so for researchers in surface chemistry, nanoscience and heritage conservation.

Fig. 2. *Bidri* zinc alloy: a) before treatment (Unpatinated surface); b) after treatment with Bidar fort clay

Another question in vogue, around this craft is the varying composition of zinc in alloys compositions, wherein there have been diverse accounts of copper concentration (Table 1), which could be attributed to the preference for alloy strength, at various sites of production. Though it has been asserted by *S. La Niece and G. Martin* [8] that the concentration of copper has to be between 2-10%, falling between the $\varepsilon + \eta$ phase field of the binary copper-zinc equilibrium diagram, at a prescribed temperature; however, this rationale has been refuted at other instances [10, 17]. Replication studies have been conclusive to indicate the significance of copper in creation of patina on the handicraft, besides affirming the role of offering strength to zinc alloy.

Table 1. Reported composition of zinc and copper, according to production sites [18]

Sr.	Location of *Bidri* handicraft production	Concentration (Ratio)			Reference if distinct than [17]
		Zinc	Copper	Others (if any)	
1.	Bidar	16	1	--	[14]
2.	Purnea	176	9	--	[19]
3.	Mushidabad	--	--	Tin (Sn)	[20]
4.	Lucknow	12 oz.	4 oz.	4 oz. Steel powder	--

Literature has been consistent to report the major ingredients for *Bidri* handicraft, as zinc, copper, castor oil, wax, copper sulphate ($CuSO_4$), silver/gold/copper engraving, sandpaper for polishing and clay from old Bidar fort walls for patination (Fig. 3) and peanut oil for lustre and polishing (the finished product) [8, 21]. Broadly, the operations of Bidri handicraft are divided into four categorical stages: a) Molding (casting), b) Carving and Inlaying, c) Oxidizing and Finishing. Electrochemical studies indicate the stability of *Bidri* handicraft surface patina, when the poultice is at pH-7 and pH-9 [22].

Method for Patina-formation

Oxidation is the most popular stage of *Bidri* production amongst scientists, owing to its unsolved mystery, and dependence on non-renewable organic clay source from Bidar fort walls. This stage poses scientific enigma for scientists and historians.

Herein, ammonium chloride (locally called as *Navsadar)* and Bidar fort clay (sieved for granular uniformity and removal of foreign elements) are blended in water in the ratio of 5:30 (Fig. 3a), and the poultice is boiled in an open iron or aluminium vessel (Fig. 3b). When the solution attains a temperature of 110-150°C, the engraved artefact (Fig. 3c) is introduced into the boiling slurry and rolled. The outcome of which is even and permanent jet-black matt-finish patina (Fig. 3d). Herein, where the zinc alloy gets jet-black patina, the non-ferrous inlay retains its contrast and lustre. It could be noted here that Bidar fort soil, can be used for 3-4 times, conditional to the size of the artefact oxidized (patinated), and the time-lag from the period of soil quarrying.

(a) (b) (c) (d)

Fig. 3. Oxidation Process of Bidri Handicraft Process: a) Addition of water for clay poultice; b) Boiling slurry on furnace; c) Rolling of artefact in boiling solution (partial patination formed); d) Finished *Bidri* product

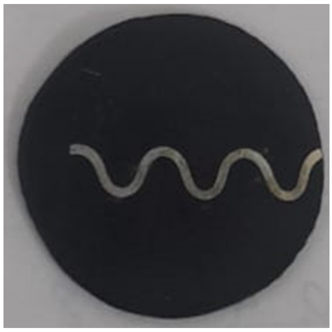

Fig. 4. *Bidri* handicraft patina-surface, with silver inlay

For the sake of current study, *Bidri* alloys of 3mm., were patinated (Fig. 4). These customized 3mm alloys, underwent traditional *Bidri* handicraft treatment method, as represented and described in figure 2; and then multi-analytical investigations were initiated.

Surface Patina of *Bidri* Handicraft

Studies characterizing composition analysis, have hinted on amalgamation of zinc and copper, along with trace elements like lead, tin, steel powder and chlorine [8, 15, 17, 20]; though there have been inconsistent indicatives on such amalgamations. Moreover, $\varepsilon + \eta$ phase of zinc and copper is widely accepted as crucial phase for 'blackening' of the surface [8], though it has also been refuted; especially with varied compositions (Table 1) practiced at distinct production sites; especially in Lucknow wherein the composition exceeded 20%; which is beyond the $\varepsilon + \eta$ phase.

Research deliberating *Bidri* alloy has been scarce; accentuating this paucity, is the presence of negligible published works on properties of *Bidar* fort soil/clay. Keeping this gap in perspective, the current manuscript presents the surface analysis of the handicraft and rudimentary investigation into the composition of the clay.

Surface Characterization

Morphological Characterization: The scanning electron microscope (SEM) surface morphological analysis exhibits dense presence of dendrite and inter-dendrite perforations/pits, an outcome of surface oxidization (Fig. 5a) built through unique presence of elements in Bidar fort clay, discussed in the subsequent part of the article.

This network of dendrites (and inter-dendrite perforations) is evinced to be characterized with copper-rich surface [15]; whereas, another study proposes that the minute size of the surface crystal structure and its acicular formation absorbs lights, which bestows the matt-black surface; rather than the existence of additional surface elements [9].

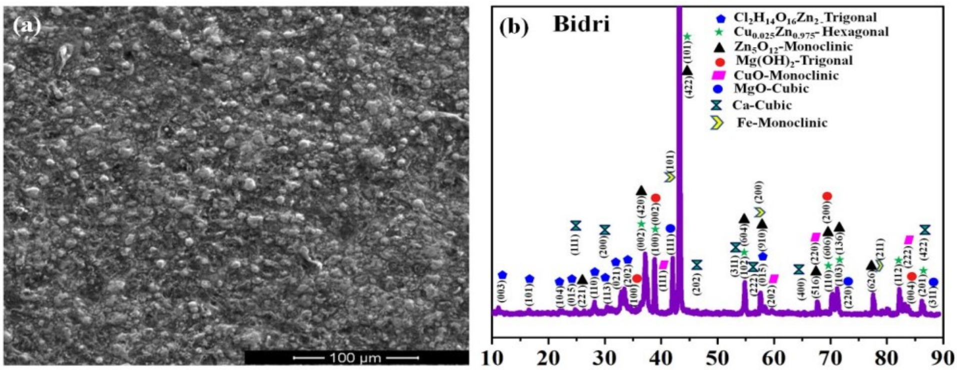

Fig. 5. a) Surface Morphological analysis using Scanning electron microscope (SEM); b) Chemical Structure using X-ray Diffraction technique of *Bidri* handicraft

Chemical Characterization

X-ray diffraction (XRD) analysis can aid investigation into the material structure of these dendrites, including atomic arrangement, crystalline size and imperfections. The XRD graph of Bidri handicraft (Fig. 5b) demonstrates distinct planes for different compositions. The *d*-spacing values of 32 peaks of *Bidri* alloy is represented. Analysis resulted in four main peaks, being identified with the elemental constituents of Zn_5O_{12}, $Cu_{0.025}Zn_{0.975}$, $Mg(OH)_2$, MgO; though traces of CuO, Ca and Fe were evident.

The mineral phases of the *Bidri* sample, with diffraction samples were identified using the Royal Society of Chemistry Supplementary Material. The results show that Zinc Oxide (Zn_5O_{12}) and Cuprous Oxide ($Cu_{0.025}Zn_{0.975}$,) were the major deposit on the surface patina, and also representing the largest crystalline size. Other elements like magnesium hydroxide, copper oxide, magnesium oxide and traces of calcium and iron were existing. The presence of iron could be partially attributed to the *Bidri* oxidation process, generally practiced by craftsmen in an iron (or aluminium) utensil/vessel (Fig. 3b and c), though presence of calcium and magnesium could be attributed to the clay, thus, indicating presence of calcium, iron and magnesium-rich deposits in the fort clay.

Surface Elemental Composition

X-ray photoelectron spectroscopy (XPS) confirmed the presence of surface zinc and copper, with major peaks at 100, 520, 922 and 1000 eV, attributed to the binding energy of Zn3p, O1s, Cu2p and respectively Zn2p (Fig. 6).

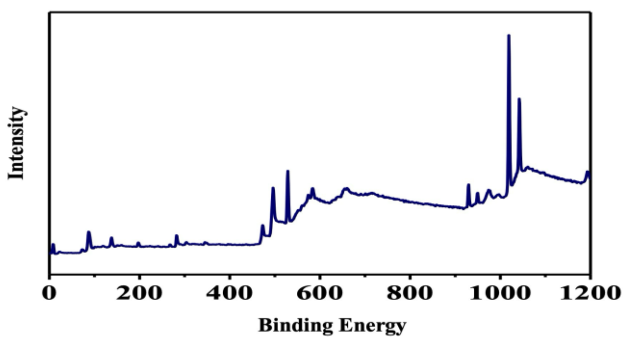

Fig. 6. Surface Elemental analysis using X-ray Photoelectron spectroscopy (XPS) technique of Bidri handicraft

The XPS spectrum demonstrates the existence of zinc and copper on the alloy surface; which is consistent with the earlier SEM, XRD analysis; and alloy / material composition inferences.

Multi-elemental Analysis

The quantitative analysis of *Bidri* patinated surface was executed using energy dispersive X-ray fluorescence (ED-XRF) spectroscopy technique; which exhibited existence of the fundamental alloys; besides traces of sulphur, potassium, calcium and iron, which is in sync with the findings of XRD and XPS (Table 2).

Table 2. Surface elemental composition, vide ED-XRF Spectroscopy

Elements	Zn	Cu	S	K	Ca	Fe
Composition (in %)	91.681	6.110	1.046	0.676	0.478	0.009

The analysis indicates presence of calcium and iron, which is indicative of clay as a source of those traces in the artefact and extends an important clue for soil analysis. Furthermore, the presence of sulphur and potassium in substantial quantities, offers another prompt for soil analysis, especially when it is compared with common clay samples.

Preliminary Clay Analysis

Analysis of soil samples vide Scanning Electron Microscope (SEM) was materialized owing to the clay capability to oxidize the artefact, iteratively. It was recognized that the Bidar fort clay loses its ability to bestow the black sheen (i.e., oxidize) after a few uses (Fig. 7).

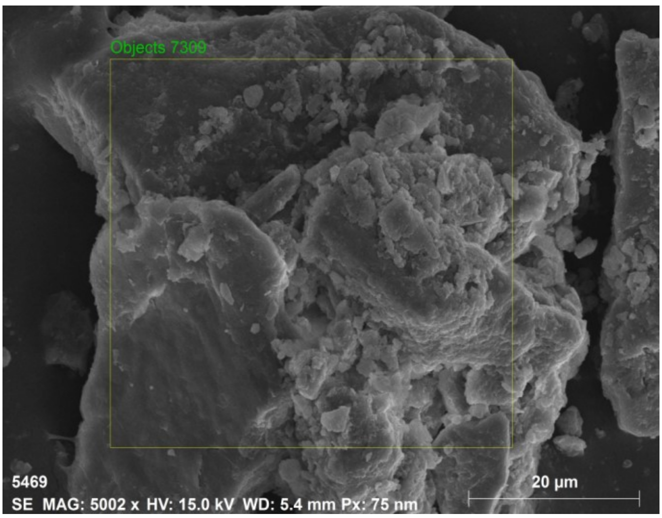

Fig. 7. SEM analysis of "unused" Bidar fort clay

Morphological analysis represents the structure of (unused) clay as granular (Fig. 7). The energy-dispersive X-ray spectroscopy (EDS) analysis (Fig. 8) report of unused clay contains silica, aluminium, magnesium, iron, antimony, carbon and sulphur in their elemental and oxide forms.

This derivation is illustrative of participation of these elements with surface active sites of the zinc alloy mould, through electroless surface reactions with available surface atoms of zinc and copper.

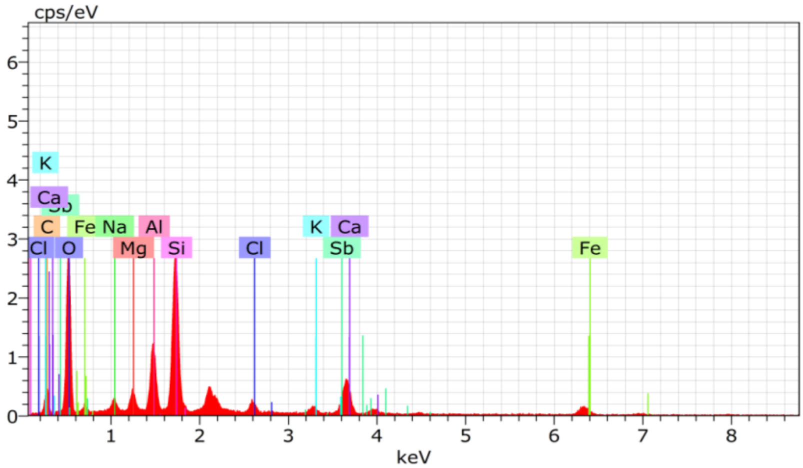

Fig. 8. EDS Report of 'unused' soil

The investigation also revealed that the clay sample was distinct on parameters of presence of chloride and rare minerals like antimony, indium, barium and traces of gold (Table 3). Furthermore, when compared with broad (general) soil compositions, the Bidar fort clay was rich in calcium, iron, magnesium, and carbon, which supports the XRD and ED-XRF spectroscopy. Thus, initial investigations are indicative of the fact that Bidar fort soil is distinct on specific parameters of elemental composition; besides its ability to oxidize metal. It becomes essential for a detailed study on the corrosive, oxidative and erosive properties of the alloy and Bidar fort clay.

Table 3. EDS Elemental composition and concentration of 'unused' and 'one-time used' soil

EDS Elemental Report			**Bidar Fort Clay**	
El	Series	AN	norm. C [wt. %]	Atom. C [at. %]
Oxygen		8	40.02	53.26
Silica	K-series	14	14.46	10.96
Carbon		6	10.39	18.42
Antimony	L-series	51	9.00	1.57
Calcium		20	8.11	4.31
Iron		26	5.98	2.28
Aluminum		13	5.76	4.55
Magnesium	K-series	12	1.75	1.53
Chlorine		17	1.54	0.93
Potassium		19	1.49	0.81
Sodium		11	1.49	1.38
		Total	100.00	100.00

The nascent scrutiny of soil portrays skeletal composition, when categorically explored has the capacity to put the enigma around *Bidri* art to rest. Furthermore, the power of the soil and alloy, can aid to advance corrosive science and surface studies, which can assist in devising methodologies to conserve zinc alloys, and also to preserve monuments. The current study makes a prelude to future studies, which is a humble step towards preserving dying crafts like *Bidri*.

Results and discussion

The preceding discussions had characterized *Bidri* craft on several parameters, which shares sufficient evidence of its heritage value. Though, oxidative abilities of the clay have been the prime enigma; the alloy composition, isotopic identities and sourcing of zinc alloy, surface patina composition and other scientific riddles are to be answered.

The current manuscript brings to focal the characterization of the *Bidri* surface that is a dense network of dendrites and inter-dendrites perforations, with copper-rich surfaces, along with traces of magnesium-oxides, iron and chlorine. The indication of copper-rich deposits on these dendrites warrants a detailed study that may offer a substantial explanation for the ratio of zinc:copper composition; so that knowledge of material science and alloy studies could be advanced, besides conserving the handicraft in question. Moreover, on comparison of results on patina by multi-analytical method, specifically with clay EDS elemental analysis, it is reported that potassium, calcium and iron are common, which might be indicative of the surface oxidative properties of these four elements with zinc alloy.

Decisively, primal to the conservation of *Bidri* is replication studies to develop methods for creation of surface patina, discussed in earlier sections. The synthesis with concoction of potassium, calcium and iron, could be tried to decipher their effect on the surface. The current manuscript has extended a foundational premise by soil characterization which could be further extended with elaborate studies [8]. Momentous and immediate steps towards conserving intangible culture have to be initiated for keeping the handicraft thriving. Social scientists could contribute by protecting the age-old operational and design knowledge, in the area of this metallurgical handicraft by detailed documentation and knowledge conservation initiatives. Conclusively, the conservation of *Bidri* handicraft calls for consolidated efforts of basic, applied and social sciences to emerge multi-pronged method to preserve the traditional craftsmanship.

Conclusions

The characterization of *Bidri* handicraft surface and its input clay using various analysis techniques have been one of the initial works in the area. The investigations were conducted in order to understand the effect of clay on the zinc alloy surface which is indicative of the oxidative properties of the clay. Elemental analysis indicates presence of potassium, calcium and iron which could be the active elements of reaction on the surface.

The XRD patterns affirm the presence of Zn and Cu in nano-dendrites, owing to their larger surface crystal structure and composition. The particle-size analysis of XRD, when correlated with SEM images demonstrate the presence of nano-metric sizes of Cu and Zn, with larger zinc particle size and larger surface concentration of copper.

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References

[1] P.C. Jones, **Philostratus Apollonius of Tyana,** 3 volumes, Leob Classical Library, London, 2005-2006.
[2] P. Craddock, A. Giumlia-Mair, *9 - śmn-Km, Corinthian bronze, shakudo: black-patinated bronze in the ancient world,* **Metal Plating and Patination, Cultural, Technical and Historical Developments,** (Editors: S.L. Niece and P.T.Craddock), Butterworth, London, 1993, pp. 101-127, https://doi.org/10.1016/B978-0-7506-1611-9.50013-3.
[3] A. Raj, A. Johari, P. Phukan, R. Menon, ***Chronicles of Bidri,*** First edition, National Institute of Design, Gandhinagar, 2018, pp. 1-18.
[4] A.K. Biswas, *The Primacy of India in Ancient Brass and Zinc Metallurgy*, ***Indian Journal of History of Science,*** **28**(4), 1993, pp. 310-315.
[5] I. Alam, *The history of zinc and its use in pre-modern India,* **Studies in People's History, 7(1),** 2020, pp. 23-29.
[6] V.N. Misra, *Excavations at Balathal, District Udaipur, Rajasthan (1995-97), with special reference to Chalcolithic architecture,* ***Man and Environment,*** **22**(2), 1997, pp. 35-59.
[7] V. Shinde, G.L. Possehl, S.S. Deshpande, *The ceramic assemblage in Protohistoric Mewar (Rajashtan), with special reference to Gilund and Balathal,* **Puratattva, 32**, 2002, pp. 5-24.
[8] S. La Niece, G. Martin, *The technical examination of Bidri ware,* **Studies in Conservation, 32,** 1987, pp. 97-101.
[9] C. O'Dubhghail, A.H. Jones, *Japanese irogane alloys and patination - a study of production and application,* **Met-Chem Research,** 2009, 289-324.
[10] B. Heynes, *An Account of Biddery (Vidri) Ware in India.* **Asiatic Journal and Monthly Register for British India and its Dependencies, III**, 1817, pp. 220-222.
[11] G.S. Birdwood, **The Industrial Arts of India,** London, Chapman and Hall, 1884.
[12] E.M. Stuart, *East Indian Art Handicraft*, **Fine Arts Journal, 35**(6), 1917, pp. 402-414.
[13] K. Lal, **National Museum Collection: Bidri Ware,** New Delhi, National Museum, India, 1990.
[14] S. Stronge, **Bidri ware of India, Metal Plating and Patination,** Elsevier, 1993, pp. 135-147.
[15] T.R. Gairola, *Technical Section: Bidri Ware*, **Ancient India: Bulletin of the Archaeological Survey of India**, (The Director General of The Archaeology in India, New Delhi), **12**, 1956, pp. 16-18.
[16] F.C. Porter, **Corrosion Resistance of Zinc and Zinc Alloys,** CRC Press, Boca Raton, 1994, pp. 1-6.
[17] G. Yazdani, **Bidar: Its History and Monuments,** Nizam Government Hyderabad, London, Oxford University Press, 1995.
[18] P.T. Craddock, *Enigmas of Bidri.* **Surface Engineering, 21**(5-6), 2005, pp. 333-339.
[19] S. Muhlberger, *Ancient India,* **The Edinburgh Companion to the History of Democracy**

(Editors: B. Isakhan and S. Stockwell) First Edition, Edinburgh University Press, 2012, pp. 50-59.

[20] G. Watt, **Indian Art at Delhi, 1903: Being the Official Catalogue of the Delhi Exhibition, 1902-1903 The Illustrative Part,** Alpha Edition, New Delhi, 1903.

[21] A. Varma, *Alternative Method of Processing Bidri-ware Crafts: An electrochemical study*, **PhD Thesis,** India: Indian Institute of Technology - Madras, 2017, pp. 1-43.

[22] B. B. Mulik, V. S. Sapner, A. Khan, K. P. Rolla, A. Shelke, B. R. Sathe, *Impact of variable pH on the stability and aggregate kinetics of Bidri handicraft surface patina.* **Inorganic Chemistry Communications, 148**, 2023, pp. 110314.

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