









## Inorganic Chemistry Communications

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Short communication

# Impact of variable pH on the stability and aggregate kinetics of Bidri handicraft surface patina

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## Highlights

- The manuscript is concerning about surface patination in heritage and *Bidri* craft in metallurgical science, and surface engineering with area of handicrafts and conservation science. Moreover, the component and composites used and reported in various studies for the patination, has been elaborated.
- The present manuscript has studied the stability and robustness of the Bidri metal wares to different types of pH.
- In this study we have used buffers of different pH, to determine the effect of pH variation on the patina surface and analysed the surface for morphological and chemical changes using SEM-EDS.

- This manuscript is helpful to artisans who are working in this art and to save *Bidri* craft art.

## Abstract

Widespread use of zinc and copper for their anti-corrosive properties with their appearance and reactivity also usage of silver in a variety of scientific and consumer applications intensifies the need to document their stability in varied aqueous environments. Thus the current work records a series of experiments with variable pH (buffered), to determine the surface stability and robustness of the *Bidri* metal handicrafts in various pH environment. The traditional craft made up of a chemical composition as alloy of zinc and copper, which when treated with slurry of tap-water and specifically sourced clay, gives a characteristic black patina. Thus, the present manuscript have demonstrated the potency of this poultice with variable pH to form stable, surface patina. The poultice is evident to preferentially colour zinc alloy in neutral and acidic environment; whereas silver inlay is distorted, with increase in inter-dendrite spaces on zinc alloy, in basic environments. These results have been proven with surface analysis of 12 *Bidri* handicraft pieces using Debye-Scherrer X-ray diffraction (XRD) and scanning electron microscopy with energy dispersive analysis of X-ray (SEM-EDAX) and found out that in all cases at least one of the zinc hydroxide chloride hydrate ( $Zn_5(OH)_8Cl_2 \cdot H_2O$ ) and zinc oxide ( $ZnO$ ) exists; but they both are white and cannot account for the deep black patina. Whereas, other compounds which were identified by XRD are silver chloride and cuprite ( $Cu_2O$ ). Overall, our results under score the impact of the pH solution on the surface stability of patinated zinc alloy, and provide an insight into the significance of pH (and aqueous solution) on the perineal practice of the craft. In additionally, we have performed electrochemical studies and we conclude that unpatinated sample is electrochemically active whereas *Bidri* soil treated CuZn sample is electrochemically inactive in  $HClO_4$ ,  $KHCO_3$  and  $KOH$  solutions after the patinationie cuprite formation and patination has been stable. Furthermore, the open circuit potential observed in the CuZn patinated sample and unpatinated sample in acidic, neutral and basic medium have  $-1.0$  and  $-0.9V$ ,  $-1.1$  and  $-0.91V$  and  $-0.7$  and  $-0.5V$  vs SCE respectively under experimental conditions.

## Graphical abstract

Schematic: Effect of (4, 7, 9 and 13.5) pH on CuZn alloy surface handicraft patinated by *Bidri* soil.



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## Introduction

At present Zn-Cu based artefacts have significantly fabricated and has been patinated, the chemical constituent present and patination depends on various parameters, viz., composition of metals, temperature, and environment. In line of this, Zn has received prominence in the recent past, owing to its anti-corrosive properties.[1] More specifically zinc alloy with copper has been one of the evolving materials [2] owing to its non-corrosive and anti-microbial properties. [3] These applications are further affected by the properties such as dissolution, colloid-ability, corrosion and other such reactions in aqueous and amorphous suspensions. The surface patinas is strongly affected interior and exterior material characteristics like chlorides, oxides, hydroxides, strong acidic and basic content. Above characterisation will determine the application of zinc and its alloy, in a plethora of avenues.

Although there has been extensive research on zinc and copper separately, and their amalgamation; but investigations on Zn and Cu alloy at  $\epsilon+\eta$  crucial phase field, of the binary Cu/Zn equilibrium have been few and inconclusive. Further, investigations on the effect of pH on Zn alloy have been few[4] and those in this  $\epsilon+\eta$ crucial phase have almost been negligible. Furthermore, studies that blend the effect of pH on rate and stability of surface patination in Zn alloy has been none; so it becomes crucial for this study to prevail.

In variable acidic environments, the physical and chemical behaviors of Zn alloy and Ag can be modified, and can affect their final surface morphological, and chemical transformations in such suspensions. Since, the Zn-Cu alloy has been documented to transform within several minutes of exposure to varied emulsions[5]. The modifications have not been fully documented; especially in the case of *Bidri* handicraft, resulting in lack of knowledge on such oxidation and surface patination process. Additionally, the protection of *Bidri* handicraft and effect of environment corrosion parameters necessitate to determine with studies in the Cu-Zn alloy.

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## Section snippets

### Bidri handicraft

One of the earliest known accounts of *Bidri* handicraft is witnessed in the works of Sir Benjamin Heynes; wherein while mentioning *Biddery (Vidri)*, he admires at the progressive knowledge of Indian-community on alloys Bidri-ware is a class of inlay damascening,[6] indigenously known as *koftagiri*, made in Ag with a characteristic black surface.[7] The provenience of this handicraft is estimated to emerge in the fifteenth century, Bahmani era in the state of Karnataka, India;[8] and the art...

### Raw materials:

The raw materials required for the preparation of Bidri handicraft are Zn, Cu, sandpaper, sand from old fort containing, saltpetre (nitrogen containing compounds collectively called as saltpetre), groundnut oil, wax, copper sulphate and Ag for inlaying....

### Process:

The overall *Bidri* metal wares are manufactured in following steps: Sand casting, engraving - inlaying, and metal surface oxidation; of which the last two phases are of special interest to the current paper.

In the first step, sand moulds are used...

### Analysis

Research groups have studied for the analysis of *Bidri* soil and patinated metal surface including, Gairola et al. found that overall Bidri soil contains 14% by weight of water soluble materials together with chloride and nitrate; though they did not state about ammoniac salts present or of. urea.[12] La niece et al., postulated that zinc was present on

the surface of the alloy, dissolved by ammonium chloride, and copper became preferentially oxidised by nitrates present in the soil, to form...

## Raw material:

The experiment used a poultice of ammonium chloride, copper sulphate, potassium hydroxide, buffer pH tablets 4, 7,9,13.6, DI water and Bidri clay. The traditional handicraft method uses tap water believed to have neutral pH of 7.

*Procedure for buffer solution preparations:* 50mL pH 4 buffer solution prepared in DI water and is taken into a 100mL Beaker, and the solution was further heated to 100°C and added 20 gm ammonium chloride under stirred till it dissolve. 50 gm Bidri soil is added into...

## Results and discussion

The surface of the sample was analysed using SEM-EDAX at different magnifications; the surface shows the presence of dendrites and inter-dendritic black space typical of patinated and crafted Bidri metal surface. Interestingly, the SEM images makes it apparent that the samples are stable in acidic pH-4 and neutral pH-7 but as we move towards basic pH the surface starts to change and found more dendrites, which is visible in pH-9.2 treated samples. The dendritic surface gets completely distorted ...

## Conclusion

Herein, the present manuscript has studied the stability and robustness of the Bidri metal wares to different types of pH. The Bidri metal ware has characteristic black patina. In this study we have used buffers of different pH, to determine the effect of pH variation on the patina surface and analysed the surface for morphological and chemical changes using SEM-EDS. The XRD studies have showed the planes of pH-7 matched to original Bidri whereas pH-4, pH 9 and pH 13.5 formulations having...

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper....

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## References (17)

H. Kabir *et al.*

[Recent research and progress of biodegradable zinc alloys and composites for biomedical applications: Biomechanical and biocorrosion perspectives](#)

Bioact. Mater. (2021)

R. Yue *et al.*

[In vitro cytocompatibility, hemocompatibility and antibacterial properties of biodegradable Zn-Cu-Fe alloys for cardiovascular stents applications](#)

Mater. Sci. Eng. C. (2020)

A.K. Neufeld *et al.*

[The initiation mechanism of corrosion of zinc by sodium chloride particle deposition](#)

Corros. Sci. (2002)

S. Niu *et al.*

[Global patterns and substrate-based mechanisms of the terrestrial nitrogen cycle](#)

Ecol. Lett. (2016)

K.L. Wilde *et al.*

[The Effect of pH on the Uptake and Toxicity of Copper and Zinc in a Tropical Freshwater Alga \(\*Chlorella\* sp.\)](#)

Arch. Environ. Contam. Toxicol. (2006)

S. La Niece *et al.*

[The technical examination of Bidri ware](#)

Stud. Conserv. (1987)

G.C.M. Birdwood, [The Industrial Arts of India](#), Google Books....

D.R. Stuart

## Petrarch's Indebtedness to the Libellus of Catullus

Trans. Proc. Am. Philol. Assoc. (1917)

There are more references available in the full text version of this article.

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### Cited by (1)

#### [SURFACE PATINA AND CLAY CHARACTERIZATION: MULTI-ANALYTICAL INVESTIGATIONS INTO BIDRI HANDICRAFT ↗](#)

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