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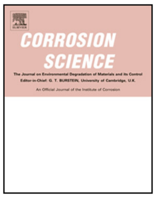

# The protective role of hydrozincite during initial corrosion of a Cu40Zn alloy in chloride-containing laboratory atmosphere

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## ABSTRACT

Hydrozincite, $Zn_5(CO_3)_2(OH)_6$, was recently found to play a key role in reducing corrosion product flaking on Cu–Zn alloys. A fundamental study was undertaken to explore the underlying mechanisms, in particular why hydrozincite can suppress the interaction between chlorides and the alloy surface. Hydrozincite could be formed by exposure of Cu40Zn to air at 70% relative humidity and 1000 ppm of $CO_2$ resulting in a surface of decreased wettability. Its presence reduces the initial spreading ability of NaCl-containing droplets and lowers the overall initial corrosion rate when the alloy is exposed to pre-deposited NaCl and wet/dry cycles.

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## 1. Introduction

Copper and copper alloys form a large group of important materials for constructional and industrial applications, with characteristic features ranging from mechanical and physical properties, over visual appearance to high corrosion resistance in a broad range of liquid and atmospheric environments. Brass is a copper-alloy family primarily consisting of copper and zinc that exhibit good strength and ductility. Based on the proportions between zinc and copper the brasses can be further classified into subgroups with different properties [1]. $\alpha$-brass with up to approximately 35 wt% zinc consists of only one phase with face-centered cubic crystal structure. $\alpha/\beta$-brass (also called duplex brass) consists of 35–45 wt% zinc and contains $\alpha$-phase dendrites with a $\beta$-phase, having a body-centered cubic structure, surrounding the dendrites [2].

Extensive investigations have been performed concerning the atmospheric corrosion of copper and copper alloys in chloride-containing field or laboratory atmospheres. Cuprite ($Cu_2O$) seems always to be the initial phase in the evolution of the copper patina. The subsequent formation of nantokite (CuCl) results from the interaction of the cuprite surface with chlorides with the subsequent transformation to atacamite or its isomorphous phase paratacamite ($Cu_2Cl(OH)_3$) as the end corrosion products [3–5]. The same constituents have also been identified within the patina after exposure in laboratory conditions with humidified air and pre-deposited NaCl [6,7]. When brass containing 15 wt% Zn (Cu15Zn) was exposed in chloride-rich atmospheres [4,8,9], additional zinc-containing corrosion products, mainly amorphous zinc hydroxycarbonate, hydrozincite ($Zn_5(CO_3)_2(OH)_6$) and zinc oxide (ZnO), were observed within the patina.

The starting point for this investigation is based on a previously reported study [4,9] on the corrosion properties of copper and commercial copper-based alloys used in outdoor building applications during long-term exposures in marine atmospheric environments. It was found that the single phase Cu15Zn alloy exhibits lower tendency for corrosion product flaking than bare Cu and a bronze (Cu4Sn) alloy in chloride containing atmospheres [4,9]. This was attributed to the early formation of zinc hydroxycarbonate, $Zn_5(CO_3)_2(OH)_6$, which hinders the formation of nantokite, CuCl, a precursor of atacamite $Cu_2Cl(OH)_3$. The flaking process was attributed to an observed volume expansion during transformation of CuCl to $Cu_2Cl(OH)_3$.

Although the protective nature of zinc hydroxycarbonate on zinc has been thoroughly investigated by Muster et al., and explained by, e.g., surface charge and surface wetting effects [10], it was decided to undertake a fundamental study of the possible cause of the beneficial effect of hydrozincite under exposure conditions which are

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as similar as possible with those of the mechanistic flaking study mentioned above [4,9]. For this purpose a brass alloy (Cu40Zn) was chosen with a high Zn-content (40 wt%) in order to facilitate the formation of hydrozincite. This study includes both diamond polished Cu40Zn and Cu40Zn with pre-formed hydrozincite that have been exposed to a chloride containing laboratory environment through pre-deposition of NaCl followed by cyclic wet/dry humidity exposures. Another reason for chosing the dual-phase Cu40Zn alloy was the possibility to explore the influence of microstructure on corrosion initiation. The wetting characteristics and surface roughness of the differently prepared surfaces were compared. The initial evolution of corrosion products was then followed with a series of complementary analytical techniques, which include in situ infrared reflection absorption spectroscopy (in situ IRAS), light optical microscopy (LOM), scanning electron microscopy with X-ray microanalysis (SEM/EDS) and confocal Raman spectroscopy (CRM). This combination of analytical techniques permits a relative comparison to be made of the formation rate of corrosion products on Cu40Zn with and without pre-formed hydrozincite and exposed to a chloride containing atmospheric environment, in order to possibly establish the corrosion protective role of hydrozincite under conditions which are similar to those during the corrosion product flaking study.

## 2. Material and methods

### 2.1. Materials and surface preparation

A commercial Cu40Zn alloy (60 wt% Cu and 40 wt% Zn) was kindly provided by Aurubis Finland Oy. The chemical bulk composition in wt-%, based on EDS-analysis, is given in Table 1. Cu40Zn samples were cut to a dimension of 1 × 1 cm or 2 × 2 cm for microstructure characterization and wet/dry cyclic exposure. Each sample was mechanically wet ground down to 2400 grit and then diamond polished successively down to 0.25 μm. Prior to the experiments, all the samples were ultrasonically cleaned in analytical grade ethanol for 10 min and subsequently dried by cold nitrogen gas prior to storing in a desiccator overnight.

Bare copper (99.98% Cu) and bare zinc (0.2% Cu, 0.07% Ti) were prepared as described above and investigated for comparison.

### 2.2. Laboratory wet/dry cycle exposure conditions

Parallel experiments were conducted in two ways: by exposures in a climatic chamber and by exposures in a chamber for in situ IRAS (Infrared reflection absorption spectroscopy) measurements. Wet/dry cycle experiments were carried out on Cu40Zn samples with pre-deposited NaCl (4 or 0.1 $\mu g\,cm^{-2}$) and then exposed to the following cyclic exposure conditions: the first cycle 4 h (RH 90%) and 2 h (RH 0%), the second cycle 16 h (RH 90%) and 2 h (RH 0%). These cycles were repeated several times, with more detailed information on the wet/dry cyclic exposure given elsewhere [11].

NaCl (in a saturated 99.5% ethanol solution) was pre-deposited onto the surfaces by means of a transfer pipette. NaCl crystals were relatively homogeneously distributed over the surface upon ethanol evaporation. The amount of NaCl particles was weighed by a microbalance (Mettler Toledo Excellence) and normalized to the geometric surface area of the samples. Detailed information on the procedure for NaCl pre-deposition is given elsewhere [12].

**Table 1**
EDS analysis of the Cu40Zn alloy.

| Cu (wt%) | Zn (wt%) | Others, mainly S and Pb (wt%) |
|---|---|---|
| 60 ± 0.2 | 40 ± 0.2 | <0.3 |

Exposures in the climatic chamber were employed by means of a WEISS WK1000 climatic chamber. Samples with pre-deposited NaCl were attached on Plexiglas fixtures and exposed 45° from the horizontal in the chamber. The exposure of all samples started simultaneously following the wet/dry cycles described above. Each Plexiglas fixture was withdrawn after 1, 2, 6 and 14 cycles (corresponding to 6 h, 1, 3, 7 days).

Exposures during in situ IRAS measurements were performed in a chamber inside the infrared spectrometer with humidified air following the same wet/dry cycles as above. By mixing dry and wet pre-cleaned compressed air of reduced $CO_2$ (lower than 20 ppm), controlled air humidity conditions were obtained. A small flow of air with 1.17% $CO_2$ from a $CO_2$ cylinder was added into the humidity chamber to obtain ambient $CO_2$ concentration, 350 ± 50 ppm. To accelerate the formation of hydrozincite, Cu40Zn samples were pre-exposed to the humidity chamber at 70% RH and with a flow of 1000 ± 200 ppm $CO_2$. Abbreviations defined to distinguish the different samples are displayed in Table 2. Experimental details are given elsewhere [13].

### 2.3. Surface and patina analysis

#### 2.3.1. SEM/EDS (Scanning electron microscopy and energy dispersive spectroscopy)

Measurements were carried out to obtain morphology and elemental information from corrosion products formed. Surface analysis was conducted be means of a FEI-XL 30 Series instrument, equipped with an EDS system (EDAX Phoenix) with an ultra-thin windows Si–Li detector and with another EDS system: X-Max SDD (Silicon Drift Detector) 20 $mm^2$ detector (Oxford Instruments). All surface images (75% SE, secondary electrons and 25% BSE, backscattered electrons) were obtained with an accelerating voltage of 20 kV.

#### 2.3.2. SKPFM (Scanning Kelvin probe force microscopy)

Analysis was conducted to determine the surface topography and Volta potential mappings simultaneously on the same surface area, by using a Nanoscope IV AFM with facilities for Volta potential measurements in two-pass mode. The probe was PtIr-coated Si (Bruker, Germany) with a nominal spring constant of 1–5 $N\,m^{-1}$ and a resonance frequency of 60–100 kHz.

#### 2.3.3. XPS (X-ray photoelectron spectroscopy)

Measurements were performed to obtain compositional information of the surface region of corrosion products. XPS spectra were recorded at different positions using a Kratos AXIS UltraDLD X-ray photoelectron spectrometer (Kratos Analytical, Manchester, UK) with a monochromatic Al X-ray source operating at 150 W. Detailed scans of Cu 2p, Zn 2p, O 1s and C 1s were recorded at high resolution (20 eV) using the C 1s peak at 285.0 eV for charge-shift corrections.

#### 2.3.4. AFM (Atomic force microscope)

Analysis was employed to obtain the surface topography, by means of a Nanoscope Multimode 8 AFM (Bruker, Germany operating in air and using tapping mode. For these measurements a triangular silicon nitride cantilever having a tip radius of about 8 nm (TESPA) was used.

**Table 2**
Abbreviations defined for pre-treated Cu40Zn samples.

| Abbreviation | Condition |
|---|---|
| DP | Diamond polished and stored in a desiccator overnight |
| HZ3 | Pre-exposed to 70% RH and 1000 ppm $CO_2$ for 3 days |
| HZ7 | Pre-exposed to 70% RH and 1000 ppm $CO_2$ for 7 days |

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