Science of the Total Environment 472 (2014) 681–694

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Corrosion and runoff rates of Cu and three Cu-alloys in marine environments with increasing chloride deposition rate☆

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HIGHLIGHTS

- Atmospheric corrosion of Cu, Cu15Zn, Cu4Sn and Cu5Al5Zn at decreasing coastal distance
- Decreasing corrosion rates with decreasing chloride load for all materials
- Flaking of outer patina constituents for Cu and Cu4Sn at sites of high chloride load
- Significantly lower release rates compared with corrosion rates
- Comparable long term release of Cu from the alloys due to similar outermost patina composition

ARTICLE INFO

Article history:
Received 21 July 2013
Received in revised form 11 November 2013
Accepted 16 November 2013
Available online xxxx

Keywords:
Atmospheric corrosion
Chloride deposition
Corrosion rates
Patina evolution
Metal release
Copper alloys

ABSTRACT

Bare copper sheet and three commercial Cu-based alloys, Cu15Zn, Cu4Sn and Cu5Al5Zn, have been exposed to four test sites in Brest, France, with strongly varying chloride deposition rates. The corrosion rates of all four materials decrease continuously with distance from the coast, i.e. with decreasing chloride load, and in the following order: Cu4Sn > Cu sheet > Cu15Zn > Cu5Al5Zn. The patina on all materials was composed of two main layers, Cu_2O as the inner layer and $Cu_2(OH)_3Cl$ as the outer layer, and with a discontinuous presence of CuCl in between. Additional minor patina constituents are SnO_2 (Cu4Sn), $Zn_5(OH)_6(CO_3)_2$ (Cu15Zn and Cu5Al5Zn) and $Zn_6Al_2(OH)_{16}CO_3\cdot 4H_2O/Zn_2Al(OH)_6Cl\cdot 2H_2O/Zn_5Cl_2(OH)_8\cdot H_2O$ and Al_2O_3 (Cu5Al5Zn). The observed Zn- and Zn/Al-containing corrosion products might be important factors for the lower sensitivity of Cu15Zn and Cu5Al5Zn against chloride-induced atmospheric corrosion compared with Cu sheet and Cu4Sn.

Decreasing corrosion rates with exposure time were observed for all materials and chloride loads and attributed to an improved adherence with time of the outer patina to the underlying inner oxide. Flaking of the outer patina layer was mainly observed on Cu4Sn and Cu sheet and associated with the gradual transformation of CuCl to $Cu_2(OH)_3Cl$ of larger volume. After three years only Cu5Al5Zn remains lustrous because of a patina compared with the other materials that appeared brownish–reddish.

Significantly lower release rates of metals compared with corresponding corrosion rates were observed for all materials. Very similar release rates of copper from all four materials were observed during the fifth year of marine exposure due to an outer surface patina that with time revealed similar constituents and solubility properties.

1. Introduction

Copper in its pure or alloyed state forms a large group of industrially very important materials. Depending on alloying elements, the desirable properties range from high electrical conductivity, corrosion resistance, wear resistance, tensile strength, soldering and joining characteristics to appealing visual appearance. This study concerns the atmospheric corrosion of bare copper sheet and three commercial Cu-alloys exposed to four different levels of chloride deposition rates in a marine environment. As evidenced from a recent review (Sequeira,

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http://dx.doi.org/10.1016/j.scitotenv.2013.11.080

2011), the atmospheric corrosion of pure copper in chloride-dominating environments has been extensively studied whereas much less is known about Cu-alloys such as brass and bronze. Typical corrosion rates of bare copper sheet in marine environments have been reported around 1 μm y^{-1}, whereby the initial rate is higher and then declines with time due to the build-up of protective corrosion products (Leygraf and Graedel, 2000). In sheltered marine exposure conditions the evolution of corrosion products proceeds through the initial formation of cuprite (Cu_2O) which continues to grow during the entire exposure period. It continues with the formation of nantokite (CuCl) and commonly ends with atacamite or the isomorphous phase paratacamite ($Cu_2Cl(OH)_3$) as corrosion end products (Krätschmer et al., 2002). These corrosion products have all also been observed within the patina on bare copper at unsheltered marine exposure conditions, and formed in laboratory exposure conditions with humidified air and predeposited NaCl (Strandberg and Johansson, 1998). The same investigation showed the corrosion rate of copper to increase with the amount of deposited NaCl and with relative humidity (Strandberg and Johansson, 1998).

More detailed laboratory studies have considered the lateral variation in surface composition and in anodic and cathodic area distribution within and adjacent to individual NaCl-particles deposited on bare copper (Chen et al., 2005a,c) and zinc (Chen et al., 2008; Neufeld et al., 2002) surfaces, respectively. Spreading of the electrolyte turned out to create the formation of galvanic elements with a potential gradient between the central area of the droplet at the NaCl particle (the anodic area) and a so-called secondary spreading area at the periphery of the droplet (the cathodic area). The interplay between acidifying gases involved, SO_2 or CO_2, and the secondary spreading phenomenon turned out to be highly complex and dependent on the concentration of the gases involved. Corrosion products observed on copper at these conditions include Cu_2O, $Cu_2Cl(OH)_3$ and brochantite ($Cu_4SO_4(OH)_6$) and on zinc zincite (ZnO), hydrozincite ($Zn_5(CO_3)_2(OH)_6$) and simonkolleite ($Zn_5Cl_2(OH)_8 \cdot H_2O$). A limited number of more detailed studies on the influence of chlorides on Cu-alloys have been reported. By exposing a bronze (Cu20Sn5Pb) alloy to humidified air with both chlorides and NO_2 present it was found that NO_2 could act as a catalyst during the corrosion process resulting in a synergism between chlorides and NO_2 on the corrosion kinetics (Cao et al., 2009). CuCl, cassiterite (SnO_2) and lead oxide (PbO) were identified as the main constituents of the corrosion products. The same bronze alloy was also exposed to chlorides and bisulfite (HSO_3^-) ions, in which a synergistic effect between the ions was observed (Cao and Xu, 2006).

When exploring the fundamentals of chloride aerosols and their influence on the atmospheric corrosion of metals, the varying exposure conditions at marine sites add in complexity. In a series of papers, Cole et al. (2009, 2003, 2004) have developed a holistic model aiming at understanding the fundamentals of marine aerosols and their influence on corrosion of primarily zinc at different distances and conditions from the ocean coastal line. The important parameters that are considered are the production, transportation and deposition of aerosols, and factors that may influence the size and chemistry of aerosols. Morcillo and co-workers have reported another set of papers, (see e.g. Feliu et al., 1999; Morcillo et al., 2001), in which different parameters have been analyzed that may influence the deposition rate of chlorides on various metals. An interesting finding from both sets of papers is the conclusion of at least two decay functions of the chloride deposition rate versus distance from the coastal line, corresponding to two different sources for producing the aerosols, breaking surf and ocean whitecaps. Over the first 500 m from the coast the chloride deposition is initially very high but decays rapidly, whereas the decay from about 2 km and inward is lower closer to the coast and decreases less rapidly.

This study is part of a long-term project with an international industry consortium that aims at assessing and generating a comprehensive understanding of atmospheric corrosion and metal release processes of copper and copper-based alloys used in building applications. In this sub-project, bare Cu and three bare commercial Cu-based alloys (Cu15Zn, Cu4Sn and Cu5Al5Zn) have been exposed at unsheltered conditions for up to three years at four marine test sites in Brest, France, representing four distances from the coastal line with a large span in chloride deposition rates. The aim is to provide a unique understanding of the rate of patina formation and coloration of copper and copper-based alloys and how they are influenced by alloying elements and chloride deposition rates. The four test sites are characterized with respect to their predicted corrosivity following the ISO 9223 classification system (ISO, 2012a) and compared with measured rates at all sites. Changes in visual appearance and evolution of patina coloration are discussed in relation to patina constituents and characteristics. Differences in metal runoff are further discussed in relation to patina constituents at one of the sites with strong chloride influence.

The importance of exploring the influence of chlorides on atmospheric corrosion rates of metals is also justified by the prediction that future corrosion rates, at least in Europe, will be more dominated by chlorides in coastal or near-coastal areas than today because of the expected increase in relative importance of chlorides on corrosion effects with increasing temperature (Tidblad, 2012).

2. Experimental

2.1. Materials and exposure conditions

Copper sheet, Cu4Sn (96 wt.% Cu and 4 wt.% Sn), Cu15Zn (85 wt.% Cu and 15 wt.% Zn), and Cu5Al5Zn (89 wt.% Cu, 5 wt.% Al, 5 wt.% Zn, 1 wt.% others) were exposed at outdoor unsheltered conditions (45° and 90° from the horizontal, facing south) at the marine site of Brest, France, for 3 and 6 months, and 1, 2 and 3 years (starting from Nov 2009). Information on bulk alloy composition of the exposed materials is given in Table 1. Four different sites of increasing distance from the coastal line in the Brest region, France were selected (site 1 — Military harbor: <5 m; site 2 — St. Anne: 20–30 m; site 3 — St Pierre: 1.5 km; site 4 — Langonnet: 40 km). The location of the sites is shown in Fig. 1. Daily deposition rates of chlorides were measured with the wet candle technique on site following the ISO 9225 standard (ISO, 2012a). Measurements of temperature and relative humidity were also performed.

Samples were exposed at each site at different periods for ex situ surface analysis and corrosion rate measurements. Metal runoff measurements were performed on single sided samples sized 300 cm^2 at site 2, an exposure initiated prior to the corrosion rate and patina formation study (Cu sheet: June 2004; the alloys: Nov 2007). All samples were exposed as-received (to mimic commercial surfaces) after surface degreasing with acetone/isopropyl alcohol and drying with cold nitrogen gas. More detailed information is given elsewhere (Goidanich et al., 2011).

Cross-sections of the exposed samples were prepared by embedding the samples into a conductive polymer followed by polishing with 0.25 μm diamond paste and subsequent polishing using OP-S suspension (Struers A/S, Denmark) and water for 15 min to obtain a near mirror like cross-sectional surface.

2.2. Corrosion rate and metal runoff measurements

Continuous sampling of metal-containing runoff water was conducted on single sided surfaces, inclined 45° from the horizontal facing south, following the guidelines of the ISO 17752 standard (ISO, 2012b)

Table 1
Bulk alloy composition (wt.%).

Material	Cu	Sn	Zn	Al	Fe	S	Ni	P	Others
Cu	99.98	–	–	–	–	–	–	0.02	–
Cu4Sn	96.19	3.66	0.03	–	0.004	0.004	0.02	0.07	0.023
Cu15Zn	85.36	0.006	14.58	–	0.02	–	0.02	–	0.014
Cu5Al5Zn	88.82	0.93	4.88	4.84	0.46	0.001	0.01	0.005	0.054