

Deposition of oxidation resistant zinc coatings on copper and leaded brass substrates with pack cementation process

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Copper-based alloys are commonly used in a wide range of applications. In order to reinforce their oxidation resistance they are usually coated with less prone materials. In this work the structure and the oxidation resistance of zinc coatings, deposited on copper and leaded brass substrates with pack cementation process is examined. It was found that coatings on copper substrate consist of two distinct layers corresponding to different Cu-Zn phases while the coatings on leaded brass substrate consist of a single Cu-Zn phase. Furthermore, the oxidation results showed that the coated samples have elevated oxidation resistance while bare substrates undergo severe damage.

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1. Introduction

Copper and copper alloys have excellent thermal and electrical conductivity, malleability and ductility which make them suitable for a great variety of metallurgical applications such as oxygen nozzles in steelmaking converters and slag hole in blast furnaces, along with many others continuous casting steel moulds. Moreover, copper-based alloys, as brass have been evaluated and used for a wide range of high strength and high thermal conductivity applications at elevated temperatures [1]. However, their usage at high temperatures is usually limited by severe oxidation attack. When copper is exposed in air at elevated temperatures, initially a Cu_2O film is formed on its surface. For longer exposure periods a CuO layer is formed over the previous one. The oxide film thickness increases logarithmically with time and irregularly, even at temperatures up to 100°C [2]. For further thickness increase, the growth rate of the oxide film follows a parabolic law until the oxide layers crack and spall in the surface. The corrosion process occurring on brass is usually dominated by the corrosion behavior of the copper which is the major alloying constituent in the alloy. Therefore, the corrosion products are similar with the oxidized copper, with the addition of zinc oxide at low concentration as zinc is the main alloying element of brass.

The improvement of the oxidation resistance of metallic substrates is usually achieved by the application of coatings consisting of materials with considerably lower corrosion rate, such as zinc. The Zn-Cu binary phase diagram shows that it is possible to form several intermetallic phases derived from Zn and Cu. Studies of

the above intermetallic compounds have shown that they can be candidate materials for high temperature structural applications [3]. The most widely used technique for the production of zinc coatings is hot-dip galvanizing. A novel technique suitable for this purpose is chemical vapor deposition (CVD) by pack cementation. In this case the substrates are packed together with the donor material and the chemical activator in a ceramic crucible and then are heat treated under argon atmosphere. This method shows several advantages, compared to the hot-dip galvanizing techniques, as no toxic fumes, such as white clouds of ZnO , ZnCl_2 and NH_4Cl emerged during hot-dip galvanizing, are formed during the deposition of the zinc coating while the energy consumption is much lower because the deposition in this case is accomplished at lower temperatures [4]. Moreover this method is suitable for coating substrates with complex geometry. This work aims to investigate the structure of Zn coatings deposited on copper and leaded brass substrates with pack cementation process. Furthermore, an initial assessment of the oxidation resistance of the as coated samples was made by subjecting them at elevated temperatures in air.

2. Experimental

Pure Copper and Leaded Brass were used as substrates for the deposition of the zinc coating. Firstly the coupons were cleaned and degreased with sandblast and then sized to 15 mm x 15 mm x 3 mm. Finally the substrates were polished up to 600 grid SiC paper, rinsed with dry alcohol, cleaned with acetone in an ultrasonic bath and blasted with hot air for drying. The as prepared

substrates were buried in the pack powders charged into cylindrical ceramic crucibles. The pack powder consisted of 1%wt NH_4Cl halide salt which was used as activator, 40%wt. zinc, the donor material and 59%wt. Al_2O_3 which was the inert filler material. The ceramic crucibles were sealed with particular high temperature resistant lids. The sealed pack mixtures were inserted for 1h in a drying furnace at 60°C in order to remove the remaining moisture. Afterwards the sealed crucibles were placed in a tubular argon-purged electric furnace which was preheated at 400°C which was the temperature of the coating process for 4h. After the 4 hour deposition the crucibles were left to cool down to ambient temperature without interrupting the Ar flow in the furnace.

The as coated samples together with the corresponding uncoated substrates were also subjected at 400°C in air for 24 hours in order to simulate a common aggressive environment. The samples were regularly weighted during the oxidation process every 5 hours with a high accuracy balance (Mettler Toledo ML204).

The examination of the samples, before and after oxidation, was performed with scanning electron microscopy (SEM) using a JEOL 840A SEM (20 kV), while the element distribution was investigated using an ISIS 2000 Energy Dispersive Spectroscopy (EDS) analyzer. Finally the characterization of the phases formed in the coatings was accomplished using a 2-cycle PHILIPS PW 1050 diffractometer ($\text{CuK}\alpha$ radiation) with Bragg-Brentano geometry.

3. Results

3.1. Characterization of the coating structure

The typical cross sectional micrographs of the as deposited pack coatings for every case, are presented in Fig. 1 together with the compositional profile. The coatings are characterized by high morphological homogeneity as no cracks and porous areas are detected.

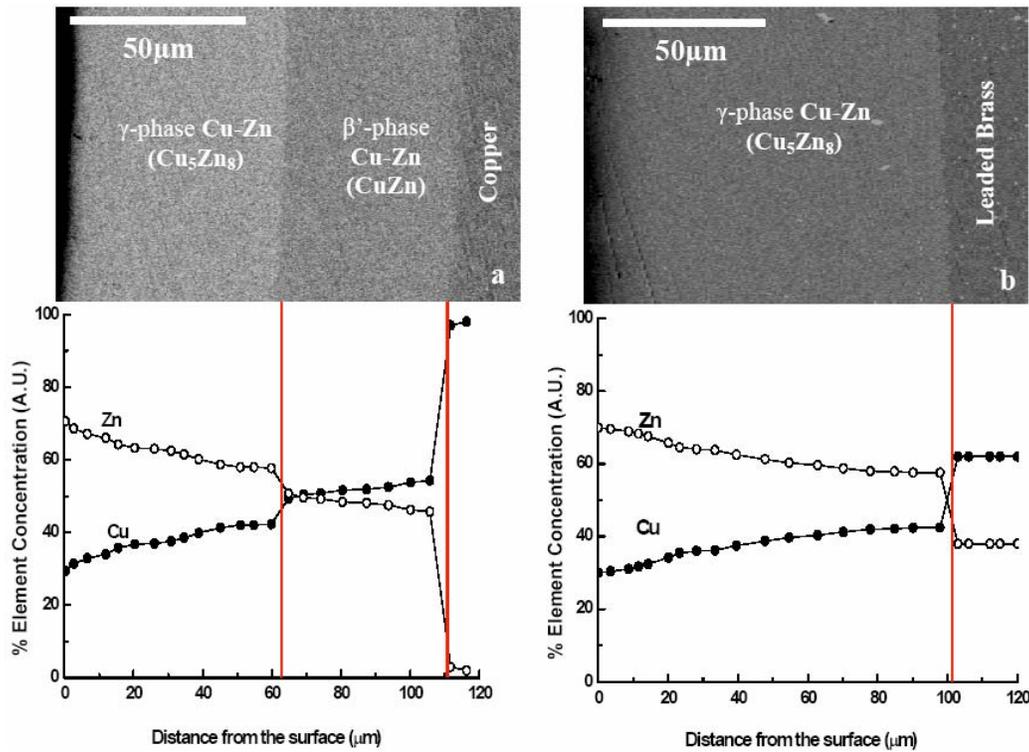


Fig. 1. Cross sectional SEM images and the corresponding EDS compositional profile of pack coatings formed on (a) copper and (b) leaded brass substrate.

Also, for both substrates the total thickness of the coatings is distinguishing elevated and is measured over $100\mu\text{m}$ in both cases which is capable for offering a significant long term corrosion protection. Particularly, it was found that the coating on the copper substrate consists of two different layers with different Zn concentration. EDS line scanning elemental analysis showed that the coating is composed only by Zn and Cu. Each layer

contains different intermetallic phases from the corresponding binary alloy Cu-Zn phase diagram [5]. Particularly, Zn concentration in the layer located in contact with the copper substrate (internal) vary between 45 to 50 wt%, while in the overlying layer (external) the same concentration vary between 58 to 70 wt% (fig. 1). The average thickness of these layers was measured at $45\mu\text{m}$ for the internal and at $60\mu\text{m}$ for the external layer.

The same elemental analysis showed that the coating formed on the leaded brass substrate has a single layer where zinc concentration vary between 58 to 70 wt% while the average thickness of the coating was approximately measured 105 μm .

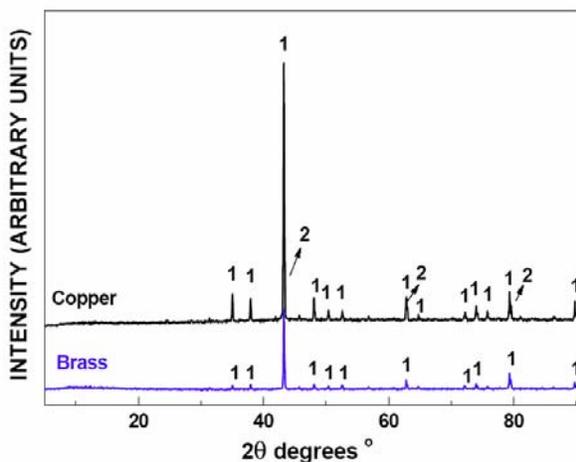


Fig. 2 - XRD diagrams of the zinc coated copper and brass substrates. Peaks denoted as #1 correspond to the Cu_5Zn_8 (γ' -phase) (Pdf# 65-6566) and peaks denoted as #2 correspond to the CuZn (β' -phase) (Pdf#65-6321) [6].

The coating structure and the exact phase identification of the two coatings were examined by X-ray diffraction (XRD) analysis. The diffraction patterns of both samples were almost identical (Fig. 2). The peaks which were mainly recorded correspond to the γ' -phase (Cu_5Zn_8) while several peaks corresponding to the β' -phase (CuZn) were also recorded in the pattern of the zinc coated copper. Considering the previous EDS results together with the XRD ones, it is concluded that the internal layer of Zn coated copper consists of the β' -phase, while the external layer consists of the γ' -phase of the Cu-Zn binary phase diagram. In the case of leaded brass the single layered coating consists only of the γ' -phase (Cu_5Zn_8). The variation of the composition through the layer thickness, which is can be attributed to diffusion rate variabilities, have not any significant effect on the phase composition of this layer as it does not give any visible differences in the SEM images while the XRD diffraction peaks are impervious from this minor elemental diversification.

3.3. Corrosion behaviour

After the deposition the samples were subjected in air for 24h at 400°C together with the bare ones. SEM micrographs of the as oxidized samples show that the coatings in both of cases were little affected from the aggressive environment and conserve most of their initial homogeneity and chemical composition (Fig. 3). In the XRD diffraction pattern (Fig. 4) of the oxidized zinc

coated copper, it was identified the presence of low intensity ZnO peaks together with high intensity ones coming from the initial identified compounds before oxidation. Similarly in the XRD diffraction pattern (Fig. 5), of the oxidized zinc coated leaded brass, the presence of low intensity ZnO peaks were also identified as oxidation product. From these experimental observations it is concluded that the overlying coating impedes significantly the penetration of oxidant agents to diffuse easily in the coating. Moreover, the result of the reaction of the top surface coating elements with the atmospheric oxygen result to the formation of ZnO which promotes the surface passivation and act as a spontaneously self formed sealer on both zinc coating.

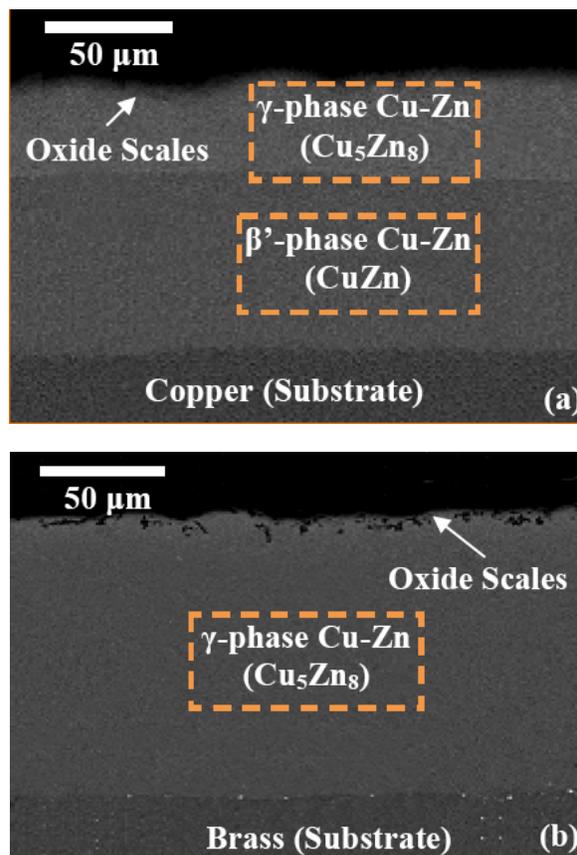


Fig. 3. Cross sectional SEM micrographs of the oxidized coated copper (a) and brass (b) substrate.

By contrast the uncoated samples subjected at the same oxidation conditions were found to suffer from severe degradation. This effect was caused by the intense attack of the oxygen anions which was further promoted from the high temperature. As a result a thick copper containing oxide layer was formed which increased exponentially with the exposure duration. The as formed scales are also brittle and successively crack and effortlessly delaminate from the substrate after reaching a certain thickness.

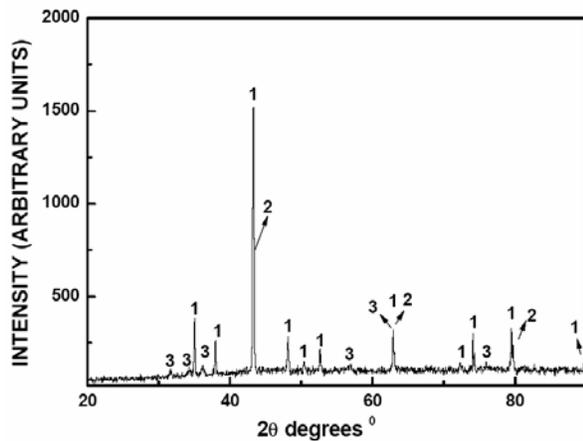


Fig. 4. XRD diagrams of the oxidized zinc coated copper. Peaks denoted as #1 correspond to the Cu_5Zn_8 phase (Pdf# 65-6566), peaks denoted as #2 correspond to the $CuZn$ phase (Pdf#65-6321) and peaks denoted as #3 correspond to the ZnO (Pdf# 89-1397)[6].

In order to estimate further the oxidation resistance of the coated samples, the mass gain versus time during oxidation was measured. The corresponding diagram (Fig. 6) reveals that in the case of coated samples the mass gain is significantly lower comparing with the uncoated substrates. This difference is attributed to the bigger amounts of oxide scales which were formed on the unprotected coupons.

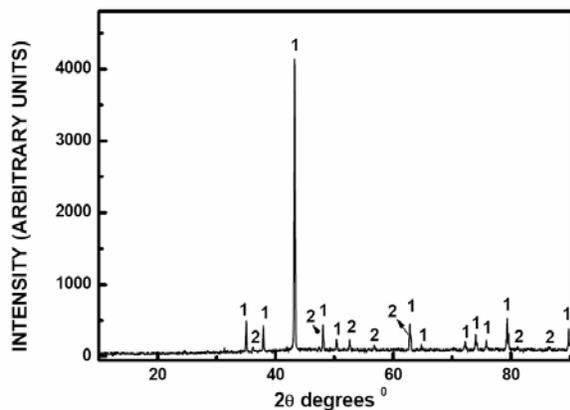


Fig. 5. XRD diagrams of the oxidized zinc coated brass. Peaks denoted as #1 correspond to the Cu_5Zn_8 phase (Pdf# 65-6566) and peaks denoted as #2 correspond to the ZnO (Pdf# 89-1397)[6].

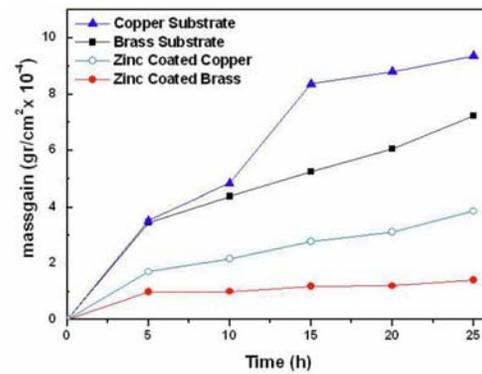


Fig. 6 - Mass gain of zinc coated and uncoated copper and leaded brass substrates during oxidation process.

4. Conclusions

Zinc was found to be a well suited metal for use as a protective coating on copper and leaded brass substrates. On both substrates, a thick coating was formed which the average thickness was measured over 100 μm . The formation of the coating is in every case the result of the good diffusivity of zinc atoms in copper and brass alloys under the particular deposition temperature [7]. The coating on the copper substrate has two layers and consist of the γ -phase (Cu_5Zn_8 external layer) and to the β' -phase ($CuZn$ internal layer). On the brass substrate a single layered coating was formed which consist only of the γ -phase. Finally both coated samples were mostly found to be unaffected by the aggressive environment in which they were subjected for 24h. The final oxidation product is zinc oxide, which also enhances the oxidation protection of the coating by passivating its surface.

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