An Effective Anti-Discoloration Coating for Copper

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This article investigated the effectiveness of a newly developed anti-discoloration method for copper (C1100). The procedure involved diffusion of aluminum into the copper substrate and the subsequent formation of Cu-Al oxide spinels on the surface by a heat treatment. Samples of C1100 with and without surface treatment were subjected to ageing at 250°C for various length of time up to 40 min in order to promote surface discoloration due to oxidation. In addition, a commercially available anti-discoloration coating (C-107) was applied on testpieces for comparative studies. Tested samples were subjected to spectral colorimeter studies in order to determine the degree of discoloration occurred on the surface; microstructures and phase identifications were examined by SEM and XRD. In conclusions, the newly developed method exhibited potential to protect the surface of C1100, and its performance surpassed that of C-107. [doi:10.2320/matertrans.M2010330]

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1. Introduction

The surface of copper can easily develop tarnish, when it is oxidized.^{1,2)} The oxidation of copper involves firstly the formation of Cu₂O, followed by reaction with O₂ as temperature increases to form CuO. So, the discoloration of copper surface is associated with the formation of Cu₂O and CuO.^{3,4)} Copper is widely used as the material for ornaments, and surface protection is required to maintain its surface appearance. There are already several coatings available to protect the copper surface against discoloration to a certain degree, e.g. C-107, which is a BTA (benzotriazole) type solution (C₆H₅N₃ base formula),^{5,6)} and ceramic coatings.⁷⁾ However, ornament manufacturers continue to search for better technique to protect the surface of copper. The aim of present study is to investigate a newly developed anti-discoloration method for copper surface, and compare its performance against a commercial coating C-107.

2. Experimental Procedure

In present study, experiments were designed to investigate the discoloration on copper surfaces with and without protections. The samples used in present study were high purity copper (C1100: >99.9 mass% Cu); C1100 plates with dimensions of 50 × 30 × 1 mm were used as testpieces; surfaces of all testpieces were sand-blasted to a roughness of RA = 0.03 μm. The testing condition to promote discoloration was set by the actual application temperature (i.e. brazing temperature) in the surrounding of copper ornament, i.e. at 250°C, and the soak time was up to 40 min. Tested samples were then subjected to spectral colorimeter studies by the BYK-Gardner Color-View System in order to determine the degree of discoloration due to oxidation on the surface. During the measurements, sample surfaces were placed flat against the circumferential illumination plate by a holder. The spectral colorimeter allowed the measurement of the color difference ΔE, which is defined by the international Commission on Illumination (CIE) as the following equation:

$$\Delta E = \sqrt{(\Delta L^2 + \Delta a^2 + \Delta b^2)}$$

Where ΔL, Δa, and Δb are color space coordination, L is the luminance, a is ranges from green to red, b is ranges from blue to yellow. The standard testpiece of pale copper color with (L, a, b) = (65.0, 26.9, 31.4) was used as the reference and scanned by the spectral colorimeter against itself to show a 1% error for the ΔE measurements. The value of ΔE was proportional to the degree of color changes on the surface of C1100; if ΔE ≤ 2.3, color difference would be un-noticeable by human eyes.⁸⁾ Each ΔE presented was an average value of 10 measurements.

To apply the newly developed protection method, firstly a mixture of 0.2 mass%/2 μm size aluminum powders in the RMA (Rosin Mildly Activated) flux was prepared. C1100 plates were immersed in 20 vol% diluted H₂SO₄ for 10 s to reveal bare metal surfaces, then washed by pure water for 20 s before immersing into this mixture of aluminum powders and RMA flux for 3 s. Samples were then heat treated at 600°C for 5 min with an atmosphere of 5 vol% hydrogen in Argon, so that Cu-Al oxide spinels could be formed on the surfaces. The optimum amount of aluminum powders and the heat treatment temperature were determined experimentally; results indicated 0.2 mass% aluminum powders and 600°C yielded the least ΔE (0.88). We have found that lower temperatures were not sufficient for aluminum diffusion to form oxide spinels. Higher temperatures actually induced oxidation of the substrate before the formation of oxide spinels. If the content of aluminum powders were below 0.2 mass%, there were not sufficient Cu-Al oxide spinels. On the other hand, excess aluminum powders on the surface yielded color changes. Three sets of samples were prepared for comparative study, (1) C1100 plates with no coating protection, (2) C1100 plates with C-107 coating on the surface, and (3) C1100 plates with Cu-Al oxide on the surface. The details of the application of C-107 coating had been outlined in a previous study.⁹⁾ All testpieces with and without protections were aged at 250°C for various length of time up to 40 min, then subjected to spectral colorimeter studies. Furthermore, microstructures and phase identifica-

Fig. 1 Spectral colorimeter studies of sample surfaces after aging at 250°C for various length of time.

Fig. 2 XRD analysis of a C1100 sample with Cu-Al oxide spinels on the surface.

Fig. 3 SEM microstructure observation of the cross-section of the C1100 sample with Cu-Al oxide spinels on the surface. (a) an edge area, (b) a central area.

tions for the surface, which contained Cu-Al oxide spinels, were examined by a Hitachi-4700 HORIBA FE-SEM and a PANalytical X'PERT PRO XRD.

3. Results and Discussions

The technique developed in this article exhibits impressive ability to protect the surface of copper against discoloration at 250°C (Fig. 1). The ΔE for C1100 without coating protection evolves from 13.58 (5 min exposure) to 22.61 (40 min exposure); for the C1100 with C-107 coating, the ΔE value increases from 7.31 (5 min exposure) to 22.15 (40 min exposure); for the testpieces protected by the new technique, ΔE is 2.01 after 5 min exposure and is gradually increased to 14.44 after 40 min exposure. Figure 1 shows that C-107 can not provide sufficient discoloration protection for C1100 at 250°C. By contrast, formation of Cu-Al oxide spinels on the surfaces of C1100 can inhibit surface discolorations. This newly developed technique uses RMA flux to protect the copper surface during the 600°C heat treatment, so the aluminum can diffuse into the copper substrate and form Cu-Al oxide spinels under the controlled atmosphere. Figure 2 shows results of XRD analysis of a C1100 sample with Cu-Al oxide spinels on the surface,

results of scanning indicate that the oxide spinels consists of CuAlO_2 , CuAl_2O_4 , CuO and Cu_2O . However, Cu peaks are also seen and this could be a result of uneven Cu-Al oxide spinels formation caused by the inhomogeneous distribution of aluminum powders prior the 600°C heat treatment. Cross sectional microstructures are shown in Fig. 3, SEM-EDS has determined regions of substrate, diffusion zone and oxide. Figure 3(a) and (b) are taken from different regions of the same sample, and inhomogeneity of the Cu-Al oxide on the surface can be observed. The Cu peaks could indicate that some regions contained insufficient Cu-Al oxide, so that they could be detected. Future work is required to investigate ways to further improve the homogeneity of Cu-Al oxide spinels on the surface. One approach is to apply ultrasonic bath during the immersion of the C1100 samples into the mixture of aluminum powders and RMA flux in order to improve the distribution of aluminum powders. In summary, the Cu-Al oxide spinels can be easily formed on the surface of C1100, and the process is relatively cheap comparing to PVD (physical vapor deposition) method, furthermore this technique not only has exhibited a potential in terms of providing anti-discoloration protection for the surface of C1100, but also can this method outperforms that of the C-107 coating.

4. Conclusions

The present study shows a method to form Cu-Al oxide spinels on the surface of C1100, so that its surfaces can be protected against discoloration. The processing procedure is relatively cheap and straightforward. Most importantly, the Cu-Al oxide spinels exhibited potential to protect the surface of C1100 against discoloration at 250°C.

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