Protections Against Surface Discoloration of Nickel Silver Plates

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In present study, a quantitative analytical approach has been taken to evaluate means to protect copper alloys (nickel silvers) against surface discoloration under the exposure of high temperatures. The aim is to propose future direction to further improve the surface protection against oxidation for nickel silver plates. Two approaches have been taken: one is to apply surface coating, another is to refine the subsurface grain structure in the bare substrate. Samples of nickel silver (C7521 and C7701) with and without surface coatings were exposed to 300°C and 350°C, respectively, for 10 min. Tested samples were then subjected to spectral colorimeter studies; phase identifications were carried out by XRD. In addition, the coating procedures were carefully studied in order to determine the optimal processing parameters for yielding the maximum protection. In conclusions, coating thickness does not affect the resistance against discoloration, pre-treatment of the substrate surfaces as well as the concentration and soak time of the anti-discoloration solutions can greatly influence the performances of the entire system against the occurrence of surface discoloration. [doi:10.2320/matertrans.M20091114]

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1. Introduction

Metal surface texture is often expressed by various feeling expressions that can be sensed by the touch of hand or reflective wavelengths received by eyes. Some materials such as architectural or artistic metals are valued by their surface textures, and others like nickel silver, which is required to possess both formability and ability to retain its silver-grey surface. Nickel silvers is a general term for copper alloys having compositions ranging from 5 to 35% in nickel content, from 50 to 70% in copper content and 15 to 35% in zinc. Nickel silver is used as materials for electrical devices and is also widely used as ornaments and the like due to beauty of its silver-gray color. Its plate form is used as caps for transistors and crystal oscillator due to the excellent deep drawing property, however, such application would expose the nickel silver cap to a temperature as high as 300°C during the manufacturing of crystal oscillator then renders the surfaces a change of surface color from silver to red-brown.1,2 This change of color is associated with the formation of copper oxides. The oxidation of copper alloys involves firstly the formation of a layer of Cu₂O, followed by reaction with O₂ as temperature increases to form CuO, as the following eq. (1). So, the discoloration of nickel silver is associated with the formation of Cu₂O (red) and CuO (black).3,4

\[ 2\text{Cu} + \frac{1}{2}\text{O}_2 \rightarrow \text{Cu}_2\text{O} + \text{O}_2 \rightarrow 4\text{CuO} \]  

The aim of present study is to evaluate means to preserve the surface silver grey color of nickel silver in a high temperature environment (@300°C) by hindering the rate of oxidation. Two directions have been taken, one is to apply protection layer or layers on the plate surfaces, the other is to refine subsurface grains in the bare condition by precision rolling. The coatings used in present study are commercial available anti-discoloration agents, C-107 and C-127 solutions from Chiyoda Chemical Co., Ltd., like BTA (C₆H₂N₃ base formula);5,6 processing parameters such as pre-coating surface roughness of plates, coating soak time and concentration of anti-discoloration solutions are studied in details followed by discussions on best practice to prevent discoloration for nickel silver plates in the future.

2. Experimental Procedure

Experiments were designed to study how to prevent discoloration (i.e. improve the oxidation resistance) for two types of nickel silver plates, C7521 and C7701, chemical composition is given in Table 1. The testing conditions were set by the application temperature/time (i.e. brazing temperature/time) in the surrounding of the nickel silver caps, i.e. at 300°C/10 min and 350°C/10 min for C7521 and C7701, respectively.

The first approach was to apply two different commercially available BTA like water-soluble anti-discoloration solutions (designated solution A (C-107) and solution B(C-127) acquired from Chiyoda Chemical Co., Ltd.) on surfaces of C7521 and C7701 plates with dimensions of 50 × 30 × 0.2 mm. The normal process of applying surface coating on nickel silver was as following: firstly immerse testpieces into 20% diluted H₂SO₄ for 10 s to reveal bare metal surface, then wash by pure water for 20 s (with and without immersing the sample in alcohol for ultrasonic cleaning for 30 s), followed by drying the surface with blow dryer, then soak the sample in the diluted anti-discoloration solution for a given time, then blow dry the surface to complete the coating process. The surface roughness of the pre-coating samples and the concentrations/soak time of anti-discoloration solution were two variables in this experiment to find the optimum processing condition. So details of how these variables change are described here; pre-
coating surface treatment: #800 and #1500 grade grinding papers were used to create two different surface roughness before applying the procedure of normal coating, the pre-coated roughness were measured by SURFTEST roughness tester. Coating parameters included concentration variations for solution A, i.e. 10, 15 and 20%, for solution B, i.e. 0.5, 1.0, 1.5%; soak time variations included 6 s, 12 s and 18 s. In addition, multi-layers of A+B (i.e. B on top of A) and B+A (A on top of B) coatings were also evaluated.

The second approach involved subjecting plates of C7521 and C7701 to precision rolling to a further reduction of 0.5% in order to refine grains in the substrate. All samples of first and second approaches were tested according to the conditions mentioned above. In addition, coating thicknesses were measured by the Fischer Isoscope, XRD were conducted to identify phases present before and after testing. Since the severe of oxidation in nickel silvers can be detected by the severity of discoloration, samples were subjected to spectral colorimeter studies in order to quantitatively determine the degree of discoloration occurred during oxidation. The results of spectral colorimeter studies are presented by the degree of spectral color change within the colorimeter diagram, i.e. the length of color change (ΔE) in the colorimeter diagram. So, the smaller the value is, the less discoloration occurs, hence the oxidation protection is more efficient. On the other words, the spectral colorimeter value ΔE is proportional to the degree of oxidation.

### 3. Results and Discussions

The importance of controlled and clean coating process is demonstrated in Fig. 1, where two samples of C7521 were subjected to the same coating A, but one process was done with thorough cleaning steps involving ultrasonic bath, the other without. The result shows that Cu oxides could be detected prior testing and hence severe discoloration (oxidation) during heat-treatment. The logic of clean process giving better coating protection is reasonable, since immersing within 20% diluted H₂SO₄ might have resulted some acid to remain within the pits made by grinding process to promote chemical reactions and discoloration, hence ultrasonic cleaning would ensure the release of trapped acid pocket, the end result is a adhesive interface between substrate and the coating. In addition, another important parameter that affects the adhesion between the coating and the substrate require particular attentions, i.e. the surface roughness prior the coating process. For C7521, two plates each had #800 and #1500 grade surface finishing and yielded surface roughness values Ra = 0.11 μm and 0.03 μm, respectively. After coating with solution A, plates were heat-treated at 300°C for 10 min, followed by spectral colorimeter measurement. The finer surface finishing, i.e. Ra = 0.03 μm yielded a ΔE value of 1.76, while Ra = 0.11 μm corresponded to a ΔE value of 3.48. So, the discoloration protection was improved significantly by finer surface finishing. This is due to a finer roughness would result more homogeneous reaction and adhesion between the anti-discoloration layer and the substrate.

Furthermore, the concentrations and soak times were varied for coating solution A and B onto both C7521 and C7701; results are summarized and presented in Table 2. Both increasing concentration and soak time could increase the thickness of the protection layer; however, there did not appear to be any correlation between thickness of the surface layer and the value of ΔE. On the other hand, to achieve the lowest value of ΔE, solution A did possess an optimal concentration at around 15% and a soak time around 12 s. Generally, solution A outperformed that of B. Hence, optimal concentration and soak time for a complete reaction with the substrate was necessary to achieve maximum protection. Interestingly, A+B and B+A double layers coating showed some promising aspects of providing better protection comparing to the single layer ones, as the ΔE values are indicated in Table 2; the mechanism associated with the improvement requires further studies.

Bare samples that were processed by precision rolling can be expected to have finer grain size, since the grain boundaries were points of preferential attack by oxidation, refining the grain structure was expected to have positive impact on improvement in oxidation resistance, as Table 2 has shown, ΔE values of tested bare samples after precision rolling for C7521 and C7701 were only 2.00 and 1.86, respectively, comparing to high ΔE values above 4 for samples prior precision rolling. The reason for C7701 to outperform C7521 was a result of lower Cu content; both of them actually performed better than some of the single-layer coated ones.

In summary, pre-coating surface roughness, coating soak time and concentration of anti-discoloration solutions can influence the performance of the protection layer. Furthermore, double layer coatings and refining grains in the substrate can further improve resistance against oxidation. By combining the precision rolling process and the coating of discoloration solution with the optimal concentration and
soak time can be expected to yield the best anti-discoloration performance and will be the next phase of study.

4. Conclusion

The oxidation resistance of C7701 is better than that of C7521, this is due to the chemical composition of C7521 has higher copper content. The thickness of anti-discoloration coatings (C-107 & C-127) can be increased by both increasing soak time (immersion time) and the concentration of the anti-discoloration agent; however, the thickness of the layer has no correlation with the degree of discoloration for the nickel silver plates. On the other hand, there exist an optimal concentrations and soak times of the anti-discoloration solutions for the best protection. The surface roughness in the pre-coating condition can influence the performance of the anti-discoloration protection, i.e. the finer the surface finishing is, the better coating performance is. Finally, refining the grain size of the substrate by precision rolling can improve the oxidation resistance in bare condition. The next phase of study will combine methods that are identified to be beneficial in present study in order to yield the maximum protection against discoloration for nickel silver plates.

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