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ARTICLE

Gold Leaf Corrosion in Moisture Acid Atmosphere at Ambient Temperature

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Abstract: Many cultural relics adhered with gold leaf (e.g. gold foil) are found damaged seriously in recent years. In this paper, gold leaf was exposed in the imitating atmosphere of moisture SO_2, NO_2 and their mixture to investigate its corrosion possibility in environment atmosphere at ambient temperature. Following phenomena were observed. The gold leaf was corroded in all these three atmospheres, which is contrary to the common sense that gold can only be corroded in aqua regia at ambient temperature. In SO_2 atmosphere, the main reason of the corrosion is the preferential oxidation of the impurity of Cu. In the atmospheres of NO_2 and the mixture of SO_2 and NO_2, the main reason of the corrosion is the combination of the preferential oxidation of the impurity and the oxidation of gold itself caused by the high defect density stemmed from the severe cold deformation during its processing. The discovery that gold can be corroded in moisture acid atmosphere at ambient temperature expands the understanding of the character of gold, and provides beneficial guidance to the protection of culture relics and modern artworks decorated with gold foil.

Key words: gold leaf (or gold foil); cold deformation; acid atmosphere; corrosion; oxidation

Gold can last thousands of years because of its chemical inertness. The high corrosion resistance of gold insures it against being dissolved in any single acid at ambient temperature. It can only be dissolved in aqua regia. In single acid environment, the electrolytic corrosion of gold has been well noticed[1-6]. It seems that gold can only be corroded in single acid under the condition of electricity at ambient temperature.

However, many cultural relics adhered with gold leaf were reported to be seriously damaged during exposure in the air. For instance, an important gold leaf decorated joss which was listed in World Heritage in 1999, the Thousand Hand Buddhism in Dazu, Chongqing, China, was reported badly damaged in recent years[7]. The joss has been placed in a cave for over a thousand years. The recent damage acceleration reminds people that the damage may have some relation to the recent change of the environment condition. Environment investigation indicated that the annual average relative humidity in the district is 82%, and that can even reaches 90% in winter or spring. In resent years, over 70% rain in the area is acid rain which causes the acid fog in the district. As a result, the surface of the gold leaf (e.g. gold foil) is frequently covered by an acid moisture film. The average pH value of the district reaches 4.16~4.46. SO_2 and NO_x are main acidity resources which could reach a content of 9.68 g/L. The average ratio between the volume of SO_2 and NO_2 in the atmosphere of the district is about 1:3[8, 9]. The gold leaf of creak and color change was observed after long period of exposure in the acid rain fog.

Although gold can not be corroded in any single acid according to common sense, the gold leaf for decoration may have special corrosion behavior. Such gold leaf underwent large amount of cold deformation before its application[10]. After the treatment with a traditional Chinese technique, the thickness of the gold leaf changes from 80 μm to 100 nm by twice cold thinning without annealing[11].

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So large cold deformation will cause very high density of crystal defects, such as vacancies, dislocations, grain boundaries and sub-boundaries. Some recent experiments proved that high density of crystal defects was formed in gold after various forms of cold deformations [12, 13]. It is well known that the crystal defects can decrease the corrosion resistance of metals for their high free energy. So it can be supported that the high density of crystal defects in the gold leaf should also have such effect on corrosion resistance.

Furthermore, gold leaves often contain a trace impurity, which will also decrease its corrosion resistance. It is reported that even platinum alloys can be corroded because of impurity[14]. Considering the high crystal defect density and impurity of the gold leaf and the observed damage, it is reasonable to consider that the gold leaf can be corroded at the environment of acid rain fog.

But there is no such report as far as we know. The research of the corrosion behavior of such gold leaf can be helpful for the protection of the culture relics, and expand the understanding of the characters of gold as well. Furthermore, the research can also provide beneficial guidance to the protection of the modern artworks decorated with gold leaf.

1 Experiment

The gold leaves were provided by Nanjing General Plant of Gold Foil and Wire, Jiangsu, China, with the average gold content of about 98 wt% (according to the producer). They were prepared with the traditional fabrication technique whose thickness was about 95 nm.

Corrosion atmospheres containing SO_2, NO_2 and their mixture were prepared with AR reagents Na_2SO_3, 65% H_2SO_4, 65%HNO_3 provided by Beijing Chemical Reagent Company, Beijing, China. SO_2 and NO_2 gases could be produced according to the following reaction equations.

$$H_2SO_4+Na_2SO_3=Na_2SO_4+H_2O+SO_2\uparrow \quad (1)$$

$$2HNO_3+Na_2SO_3=Na_2SO_4+H_2O+2NO_2\uparrow \quad (2)$$

In the preparation of SO_2, the amount of the reagents were 0.2 mol Na_2SO_3 and 0.1 mol H_2SO_4. In the preparation of NO_2, the amount of the reagents were 0.2 mol Na_2SO_3 and 0.1 mol HNO_3. In the preparation of the mixture of SO_2 and NO_2, the amount of the reagents were 0.6 mol Na_2SO_3, 0.1 mol H_2SO_4 and 0.4 mol HNO_3.

The corrosion imitation device is shown in Fig.1. The gold leaf was wound around a piece of ABS plastic supporter. The ABS supporters with gold leaf samples were hanged in a beaker which was placed on a plastic fill block on the bottom of a kettle. Then Na_2SO_3 was carefully added to the bottom of the kettle. And the reagent acids were then carefully dropped into the kettle to react with Na_2SO_3. When the reagent acids were added, resultant gas was observed. Then the kettle cap was covered and screwed up, while reaction product gas could be observed releasing through the valve on the kettle cap. The valve was closed when no releasing gas could be observed. The samples were taken out one month later for characterization. Because both the reagent acid and the reaction products contained water, the atmosphere in the kettle was acidic and moisture. Because Na_2SO_3 in the reaction was over dosed, the partial pressure of SO_2 and NO_2 in their mixture could be controlled by the amount of H_2SO_4 and HNO_3. The ratio between the partial pressure of SO_2 and NO_2 in the kettle atmosphere should be 1:3, which was the same as that in the actual atmosphere of Dazu region.

Hitachi S-3600N type SEM with EDX was applied to analyze the microstructure and surface composition of the samples. ESCALab250 type XPS, Thermo Scientific Corporation, was used to analyze the corrosion products of the samples.

The electrochemical impedance spectroscopy (EIS) was tested at the open-circuit potential obtained in the potentiodynamic scanning with a 283A type electrochemical workstation. The frequency range was 0.00～100 kHz, and the open circuit potential was 0 V. The EIS test of both the traditional Chinese gold leaf and the gold sheet was carried out with a working area of 20 mm×5 mm.

2 Results and Discussion

2.1 Microstructure and content of the gold leaf

EDX surface scanning of 3 random selected regions of the gold leaf shows that the average composition of the gold leaf is 98.14 wt% Au, 1.57 wt% Ag, and 0.29 wt% Cu. The microstructure of the gold is shown in Fig.2. Although the gold leaf is even largely, many wrinkles, tiny pits, and rough surface of the gold leaf can be observed. So it can be deduced that many crystal defects stem from the large amount of cold deformation during its process.

2.2 Corrosion results in SO_2 atmosphere

The microstructure of the gold leaf corroded in SO_2 atmosphere is shown in Fig.3. Many pits can be found through optical microscope observation. A large pit surrounded by many arc arranged lines and many little pits are shown in the SEM image.

The microstructure and EDX analysis of the gold leaf corroded in SO_2 atmosphere is shown in Fig.4. The EDX analysis was focused on the corrosion spot A of Fig.4a. The average composition of the spot A is 60.51 wt% Cu, 30.21 wt% Au and 9.28 wt% O. Therefore the corrosion products should be O containing compounds.

Fig.5 shows the XPS spectrum at Cu 2p3 region of the gold leaf corroded in SO_2 atmosphere. The peak at 933.0 eV indicates the existence of Cu^{2+}. From other spectra at S 2p, Ag 3d, Au 4f regions, it can be concluded that S exists in the form of SO_4^{2-} and no Au or Ag in ion state can be found. Therefore, the corrosion mechanism should be the prefer