Two-step method for preparing calcium oxalate film on marble surface for stone protective

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Abstract

Calcium oxalate film was prepared by a novel two-step method on the surface of the marble substrate. The seed film was coated by a chemical reaction process, providing a good connection to the marble surface. Meanwhile, calcium oxalate solution was interwoven into the seed film to form a continuous network at room temperature. The x-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis results indicated that the calcium oxalate film prepared by the two-step method showed a more intensive crystallinity degree and homogenous than that by the traditional oxalate treatment method (a scattered seed film). Subsequently, it was found such calcium oxalate film is feasible for preventing the marble substrate from chemical weathering. Furthermore, the change of the chromatic value, water absorption properties and adhesion strength of the marble substrates by the film is minimal. This method overcomes the limitations of traditional oxalate treatment process and has great potential for the protection of marble artifacts.

1. Introduction

Marble is one of the oldest materials used in the construction of different types of structures founded in many parts of the world. It represents the oldest trace of human activity, such as in artifacts dating from 700,000 to 130,000 years ago [1]. Over time, three types of factors have been observed that endanger the status of the stone artifacts, such as physical (temperature, soluble salt, wind) [2], chemical (atmospheric pollution, water) [3] and biological (lichen, bacteria) [4]. Crack and deformation, detachment, discoloration and deposits, biological colonization, loss of materials are among the most common effects of stone weathering [5].

To protect the marble artifacts, a variety of treatments have been proposed over the past century. One of the treatments that has shown promising results on marble artifacts is the use of calcium oxalate, due to its much lower solubility than marble and similar crystal structure [6]. Formation of the calcium oxalate film on the marble surface involves exposure of the stone to an aqueous solution containing molar quantities of oxalate, ammonium oxalate or diethyl-oxalate [7–9]. The reactions depend on the room temperature, the concentration of chemical solution and the application method [10–12]. D Mudronja et al evaluated the efficiency of applying ammonium oxalate for protection of marble by poultice, immersion and brushing methods, and concluded that for large surfaces the brushing treatment can be considered as an efficient method [13]. A Burgos-Cara et al demonstrated that low pH and the addition of citrate led to continuous and coherent protective layers [14]. However, these treatments are usually produced fine-grained crystals rather than thick protective film, because the low concentration of calcium ions derived from marble dissolution [15, 16]. To overcome these limitations, in this study, after a number of experiments were carried out, a two-step method for producing calcium oxalate protection film on the marble surface was proposed. The properties of the calcium oxalate film were characterized and evaluated by x-ray diffraction (XRD), scanning electron microscope with energy dispersive...
x-ray spectrometry (SEM-EDS), colorimeter, Scotch Tape Test (STT), etc, with promising results for the protection of marble artifacts.

2. Experimental

Sample preparation: All chemicals were of analytical grade and used as received. Absorbent cotton, ammonium oxalate, calcium acetate, oxalic acid and nitric acid were purchased from Aladdin-reagent Co., Ltd. Marble specimens (25 mm × 25 mm × 10 mm) were polished with SiC paper and cleaned.

In order to produce uniform coherent coating, a two-step method was investigated. The seed film was formed by using the metasomatic reaction between ammonium oxalate solution and marble substrate at room temperature. These films were then epitaxially thickened in calcium oxalate solution, in which the treatment increased crystallinity degree and coating uniformity. For the preparation of calcium oxalate seed film, absorbent cotton was soaked in 5 wt.% ammonium oxalate solution and packed onto marble surface for 24 h. For the growth of calcium oxalate film, a mixture of 2.5 mM calcium acetate, 2.5 mM oxalic acid and 0.006 mM ml−1 HNO3 aqueous solution was prepared. The calcium oxalate solution was deposited on seed film through spray gun with 1.5 mm diameter nozzle at room temperature (∼25 °C).

Characterization: The chemical composition of film deposited on marble substrate in different procedure was determined by XRD analysis with a Bruker D8 Advance diffractometer (Cu Kα radiation, 40 kV, 30 mA, angle 10°–70°, step size 0.02°) and XRD data were analyzed using Jade software. Scanning electron microscope with energy dispersive x-ray spectrometry (SEM-EDS, JSM-6700F) to characterized morphology and chemical composition before and after treatment.

The chromatic value of marble substrate before and after treatment was described by the automatic colorimeter (WSD-3C), with the standard illuminant D65 and observer at 10°. The measured parameters were L*, a*, b* coordinates (accounts for luminosity, red-green parameter and blue-yellow scope), total color difference ΔE* provided as a result of the formula ΔE* = (ΔL*)² + (Δa*)² + (Δb*)²/². Water absorption under vacuum was performed on the sample before and after treatment to evaluate the marble structure change, according to standard test UNE-EN 1936:2007, by keeping them reach saturation (%). Surface adhesion strength of the sample before and after treatment was test by Scotch Tape Test (STT) [17]. Peeling test was carried out on the surface of the stone samples to study the decrease of released material with transparent double-side adhesion tape (Deli), 2.5 cm wide 4 cm long, within 90 s of application remove the tape weighed on a laboratory balance with sensitivity 0.0001 g. Acid resistance of the sample before and after treatment was evaluated by immersion test in sulfuric acid solution (pH = 4.0, equivalent to heavy acid rain). The change of solution pH value was measured in each period (1 h, 2 h, 4 h, 6 h), and surface morphology was observed after test.
3. Results and discussion

Preparation and characterization of calcium oxalate film on the marble substrate

A schematic drawing for the coating process of calcium oxalate film is shown in Figure 1(a). Firstly, calcium oxalate solution was absorbed in cotton, which was packed on the surface of the marble for 24 h. Afterwards, seed film was formed by chemical reaction between ammonium oxalate solution and the calcium carbonate derived from marble (Sample ‘SF’). Meanwhile, aqueous calcium oxalate solution was prepared as described in the experiment section. Subsequently, the calcium oxalate solution was sprayed on seed film to obtain dense calcium oxalate film, which is very important for the protection of marble artifacts (Sample ‘PF’). Compared with the raw marble (figure 1(b)), the SEM image of sample ‘SF’ shows a discontinuous film composed of needle-like particles (figure 1(c)), which could be attributed to the limited concentration of calcium ions and driving force of heterogeneous (mainly due to dolomite) [18]. The SEM image of the sample ‘PF’ in figure 1(d) shows a continuous film composed of block crystal with micro-metric dimensions. The main chemical compositions of the protective film are Ca, C and O measured by the energy dispersive spectroscopy (EDS), as shown in figure 1(d).

The XRD spectrum of marble, sample ‘SF’ and sample ‘PF’ are presented in figure 2. Characteristic diffraction peaks of whewellite (Monoclinic, P21/c(14) space group) are found in sample ‘SF’ and sample ‘PF’. In the atmosphere, whewellite is the most stable phase of calcium oxalate. Moreover, the sample ‘PF’ shows a relative strong diffraction peak of whewellite, indicating the calcium oxalate produced by the two-step method on the marble surface has better crystallinity degree.

Property assessment of the calcium oxalate film

(1) **Water absorption**: To evaluate possible treatment-related variations in porosity, water absorption under vacuum was performed. Table 1 shows the test results of marble, sample ‘SF’ and sample ‘PF’. A value of 0.34 wt.% was obtained for the marble, and the sample ‘SF’ reached to 0.41 wt.%, while the sample ‘PF’ gave 0.42 wt.%, indicating the impact to the water absorption of the substrate after treatment is minimal. This is due to the good compatibility of calcium oxalate with marble, thereby maintain the penetration of water into intergranular spaces [19].

(2) **Chromatic aberration**: To evaluate the aesthetics influence of the protective film, the chromaticity coordinate results of marble, sample ‘SF’ and sample ‘PF’ are listed in table 1. For the calcium oxalate coated marble specimens, the overall chromatic variation is less than 2. Thus, the surface difference of the samples before and after treatment is hardly detected by visual observation [20]. These results can be related to the whitish natural color view of marble and calcium oxalate film.

(3) **Surface mass change**: The ‘Scotch Tape Test’ was performed to evaluate the bonding strength of the calcium oxalate film, as shown in table 1. For the marble sample, the weight loss is 0.12 mg cm\(^{-2}\). The weight loss of the sample ‘SF’ and sample ‘PF’ is 0.09 mg cm\(^{-2}\) and 0.18 mg cm\(^{-2}\), respectively. After film
deposition, the surface weight loss of the marble almost not changed, likely because the calcium oxalate film
and marble are both calcic inorganic compounds and they can adhere together firmly.

(4) Acid resistance: In order to evaluate the acid resistance properties of protective film, the marble, sample ‘SF’ and sample ‘PF’ are immersed in H2SO4 (pH = 4) for 6 h and then dried for 1 days under room temperature. As illustrated in figure 3, the marble surface etching severely after acid attack (figure 3(a)). While calcium oxalate coating still presented on sample ‘SF’ surface, although it looks patchy (figure 3(b)). Moreover, for the sample ‘PF’, the coating appears to be intact (figure 3(c)). Meanwhile, the variations of the sulfuric acid solution pH value in each period (1 h, 2 h, 4 h, 6 h) was measured (table 1). In the case of marble, solution pH value exhibits noticeable change (increased to 5.3), due to the dolomite react with the sulfuric to form calcium sulfide. Sample ‘SF’ appeared less affected by the immersion tests with lower variations of the solution pH value (increased to 4.7). For the sample ‘PF’, the change of pH value was negligible (increased to 4.1). Thus, the protective film offers valuable protection for marble against acid dissolution. This is attributed to the lower solubility and better acid resistance of calcium oxalate crystal.

4. Conclusions

A novel two-step method to form calcium oxalate film on the surface of the marble was prepared and investigated by the x-ray diffraction (XRD), scanning electron microscopy (SEM), colorimeter, Scotch Tape Test (STT), etc. The results indicated that the calcium oxalate film prepared by the two-step method is more homogeneous than that formed by the traditional oxalate treatments process. Through the immersion test in sulfuric acid it was found such calcium oxalate film can strongly prevent the substrate from chemical weathering. Furthermore, the intrinsic properties of marble such as the color, the water absorption property and surface weight loss were almost not changed. In summary, this two-step method to form calcium oxalate film on the marble surface overcomes the limitations of traditional oxalate treatments, demonstrates highly efficient for the protection of outdoor marble artifacts.

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