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Fractal characteristics and wettability of Nano-Al_2O_3/Ni-Co composite coating prepared by electrodeposition

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Abstract: Nano-Al_2O_3/Ni-Co composite coatings were formed on gray cast iron surface by electrodeposition method. The composite coating has a more flat surface and compact microstructure than the pure Ni-Co coating. The fractal surface structure parameters were calculated by fractal theory and the average fractal dimension is 1.301 3. The contact angles were measured and the maximum value reaches 105°. The relationship between wettability and fractal structure was explained by Cassie–Baxter equation. The results indicate that wetting behavior varies with the fractal dimension. But the change of contact angels is not directly proportional to the fractal dimension.

Key words: electrodeposition; fractal; wettability; morphology

1 Introduction

Fractal is a novel branch in the field of nonlinear science, and it is a powerful tool to characterize many complex systems quantitatively. The concept of fractals was introduced by MANDELBORT et al [1] and subsequently used to characterize technical surfaces as significant aspects of materials science and engineering. Researchers have determined the relationship between the physical quantities and fractal dimension through the use of computer image processing technology or other methods. According to preliminary dimensional analysis, an efficient dimensionless formulation was proposed to estimate the electric and thermal contact conductances across the surface fractal dimension [2]. For describing the numerical model and the contact tests, a review of influencing factors like hardness and geometrical deviations with larger wavelengths than the roughness was given by GOERKE and WILLNER [3]. Furthermore, a statistical model used to simulate the size-scale effects on strength and toughness of brittle and quasi-brittle materials was also proposed [4−5].

Wettability between liquid and solid surface is governed by two factors, namely, the chemical component and the geometric structure [6−7]. It has been well-known that fractal structures can effectively magnify the real surface area compared with the projected one, and then enhance the wettability of a solid surface. Since super water-repellency has attracted much attention, many methods have been employed to produce such rough surfaces [8−12].

In previous work, super water- and oil-repellent surfaces [10−11] with fractal dimension of 2.19 were made of anodically oxidized aluminum surfaces treated with fluorinated compounds of low surface energy and super water-repellent poly (alkylpyrrole) films [12] with a fractal dimension of 2.23 were electrochemically synthesized.

The water-repellent coatings were successful prepared by a composite electrodeposition process. The contact angles were measured by water liquid on the coating surfaces, and the wetting behavior varied with the fractal dimension.

2 Experimental

The gray cast iron samples were cut into 20 mm×20 mm×5 mm. The basic parameters of alumina were the average particle size 60 nm, the purity not less than

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99.99%, and the specific surface area (180±10) m^2/g. Watt plating solution was the earliest application and the most extensive of nickel plating solution. It consisted of three basic components, nickel sulfate, nickel chloride and boric acid.

To ensure the nanoparticles to form a homogeneous suspension in the electroplating bath, the sonication was used for 120 min. In the process of electrodepositon, the technology parameters were determined: the current denisty was 40 mA/cm^2, the temperature of electrolyte was 45 °C, the content of nano-Al_2O_3 in electrolyte was 20 g/L (see Table 1), and the mixing was mechanical stirring together with ultrasonic vibration. The morphology of nanocomposite coating surface was observed using SEM (JSM−5500LV, Japan electronic), and the 3-D morphology was observed on a laser co-focusing microscope. The wettability of composite coating surface was determined by measuring the static contact angle of a water droplet (2−3 mm diameter) using Interface Tension/Contact Angle Measure Equipments (JC2000A, Powereach, China). The experimental temperature was 20 °C.

Table 1 Component of electroplating bath

$\rho(NiSO_4\cdot 6H_2O)$/ $(g\cdot L^{-1})$	$\rho(NiCl_2\cdot 6H_2O)$ /$(g\cdot L^{-1})$	$\rho(H_3BO_3)$/ $(g\cdot L^{-1})$	$\rho(C_7H_5NO_3S)$/ $(g\cdot L^{-1})$
280	40	35	0.1−0.2

3 Results and discussion

3.1 Microstructure of Nano-Al_2O_3/Ni-Co composite coating

Figure 1 shows SEM image of pure nickel cobalt coating, while that of Nano-Al_2O_3/Ni-Co composite coating is given in Fig. 2. Compared with Ni-Co coating, the size of crystal grains in the Nano-Al_2O_3/Ni-Co nano-composite coating largely decreases due to the dimension effect of nanoparticles. Grain growth driving force is related to different curvatures of grain boundary in course of grain growth according to crystallization theory. The total driving force reduces the interfacial energy, so the grain boundary is always toward the center of curvature direction. Moreover, grain growth resorts to the large angle grain boundary migration. All the factors affecting grain boundaries migration also influence grain growth. Nickel grains normally grow in course of preparing pure Ni coating, which proximity grain boundary migrates and interconnects into a straight junction, meanwhile, the interfacial energy reaches to 0 and grain grows fully. Nanoparticles apparently obstruct grain boundary migration in preparing nanocompsite coatings. Moreover, the obstruction behaviors become obvious when the amount of particles increase and size decreases. The high active surface of nanoparticles provides an amount of nucleus for Ni atoms in the electrodeposition process. The composite coating with a fine and compact microstructure was obtained because of a higher nucleation rate.

3.2 Calculated fractal dimension of composite coating

For fractal characteristics analysis, 11 surface contour line data were collected, then the fractal dimensions were calculated by fractal Bronian motion method given in Table 2. At the same time, the fractal character was evaluated according to the results.

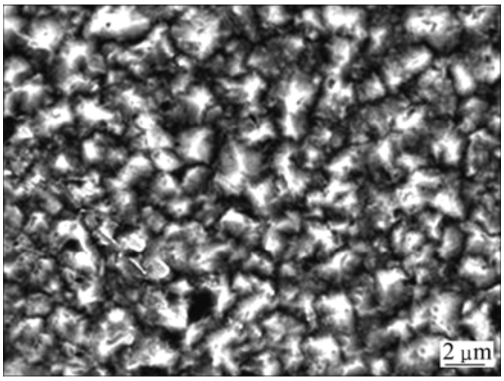

Fig. 1 Pure nickel cobalt coating surface morphology

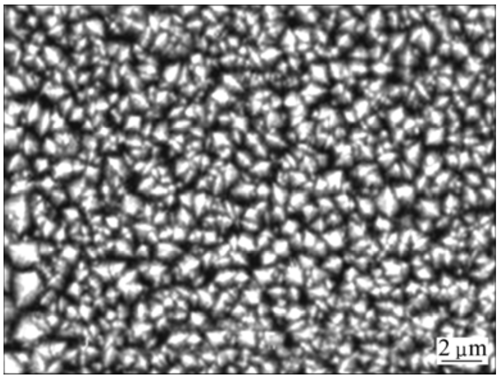

Fig. 2 Nano-Al_2O_3/Ni-Co composite coating surface morphology

Table 2 Results of fractal dimension

No.	Fractal dimension (*D*)
1	1.347 8
2	1.267 9
3	1.223 9
4	1.440 8
5	1.296 9
6	1.302 2
7	1.291 4
8	1.183 9
9	1.300 6
10	1.322 6
11	1.336 3

The surface contours data were calculated, and all the values are large than 0.99. Therefore, the composite coating has a distinct fractal character. The fractal dimension D is between 1.183 9 and 1.440 8. Moreover, an average fractal dimension is 1.301 3. The surface contour is simulated as shown in Fig. 3 by fractal Bronian method. Figure 4 shows the point cloud values of fractal dimension, and the slope is H.

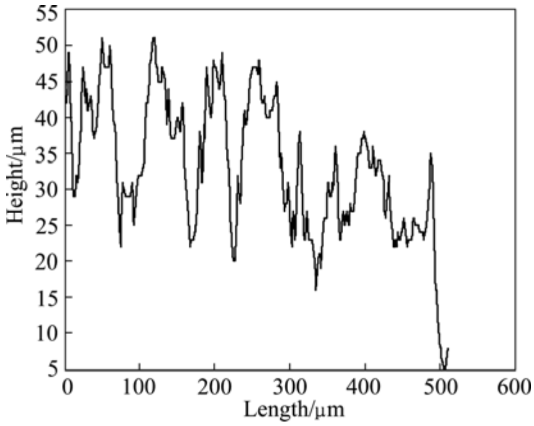

Fig. 3 Surface contour line simulated

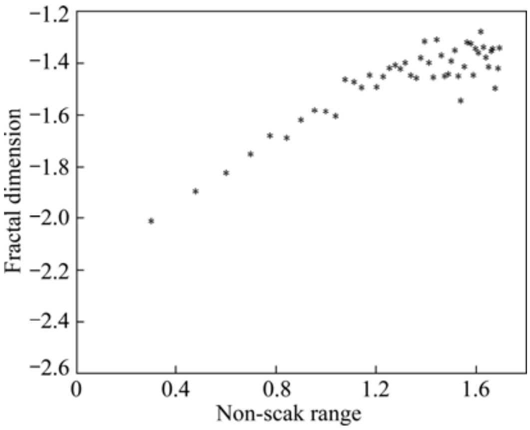

Fig. 4 Fractal image of Fig. 3

3.3 Wettability and fractal characteristics

Figure 5 shows the contact angle of different coatings. Surface wetting property relies on the surface structure. The wetting property of the coating is investigated by contact angle measurement. It is found that when the microscale bumps are used to form coating, the surface is highly hydrophilic with a contact angle (CA) of about 105°. Based on the morphology shown in Fig. 2, it is believed that the electrodeposited composite coating has many vacancies among individual nanostructures enough to trap air [13−15].

To understand the origin of the observed high hydrophobicity, the CA in terms of the Cassie–Baxter equation [16], cos θ_r=f_1, cos θ_0−f_2, in which f_1 and f_2 are the fractions of solid surface and air in contact with liquid, respectively; θ_r and θ_0 are the CAs on the

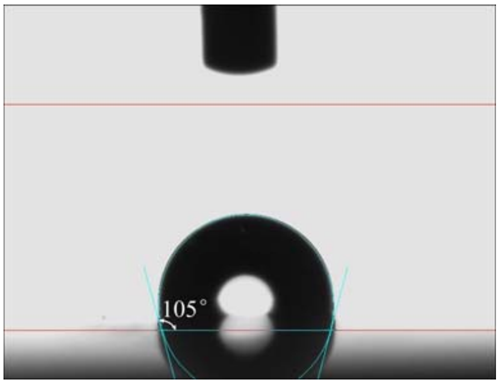

Fig. 5 Contact angle measurement at interface with NPSi film (contact angle is 105°)

bionic surface (105°) and on the fine and compact surface (43°), respectively. Since f_1+f_2=1, and f_1 is calculated to be 0.43. The low value of f_1 suggests that the microscale bumps and nanoscale asperities on the surface of these bumps are responsible for the high hydrophobicity.

Furthermore, Fig. 6 shows the confocal laser scanning microscopy images of the composite electrodeposition coatings, which provides further insight into the microstructure characteristics inside of the fractal structure. When the structure of the roughness is in fractal nature, the Wenzel equation θ_R=Rcos θ is rewritten as [11]

$$\cos \theta_f = (L/l)^{D-2} \cos \theta \quad (1)$$

where L, l and D are the upper and lower limits of length of the fractal (self-similar) structure and the fractal dimension, respectively [17]. The roughness factor, R, can be expressed as $(L/l)^{D-2}$ in the case of fractal surfaces. Then, the fractal dimension of the cross section, D_{cross}, is measured by the box counting method to be 1.30 in the range between l=0.12 μm and L=26 μm (see the inset in Fig. 3), below and above the range, D_{cross} is found to be unity. Thus, the fractal dimension of the surface has

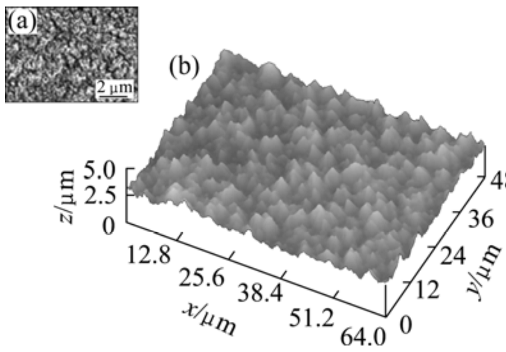

Fig. 6 LSCM measurement of morphology of composite electrodeposition film

been evaluated as D=D_{cross}+1=2.30. According to Eq. (1), $R≈(L/l)^{D-2}$ was calculated to be 3.342. Because some liquids show the repellent property (θ_R >90°) on the rough surface in spite of the wettable one (θ<90°) on the flat surface, this result is quite curious if the measured contact angles are the equilibrium values. The result is presumed that the difference between experimental data and theoretical calculation is due to the fractal structure formed in the deposition process rather than the roughness of substrate.

4 Conclusions

1) Nano-Al_2O_3/Ni-Co composite coatings were successfully prepared by electrodeposition process. The surface of composite coatings is flat and the microstructure is found to be more compact than that of the pure Ni-Co coatings.

2) The fractal surface structure parameters were calculated by fractal theory, and the average fractal dimension is 1.301 3.

3) The maximum value of the contact angle reaches 105°. The relation between wettability and fractal structure was explained by using Cassie–Baxter equation. The wetting behavior varies with the fractal dimension. However, the variation of contact angels is not directly proportional to the fractal dimension.

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电沉积 Nano-Al_2O_3/Ni-Co 复合涂层的分形特征及润湿性

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摘 要：采用电沉积的方法在灰铸铁表面制备了 Nano-Al_2O_3/Ni-Co 复合镀层。与纯镍涂层相比，复合镀层表面平整、细致。运用分形原理计算了分形表面的结构参数，分形维数为 1.301 3。测量了接触角，其最大值达到 105°。运用 Cassie–Baxter 方程解释了润湿性与分形结构的关系。结果表明：随着分形维数的变化润湿角而变化，但是接触角的变化与分形维数的比率并不呈现线性关系。

关键词：电沉积；分形；润湿性；形貌

(Edited by LI Yan-hong)