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表面活性剂对电沉积 TiO_2/Ni 复合镀层的影响

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摘 要：研究了表面活性剂对纳米 TiO_2 在镀液中的分散行为和沉积行为的影响，结果表明十六烷基三甲基溴化铵(CTAB)对纳米 TiO_2 颗粒的分散效果显著，镀液 40 min 内不发生明显分层。相比其他表面活性剂，由于纳米颗粒在涂层中均匀分散，CTAB 分散的镀层显微硬度最好，且热稳定性好，孔隙率显著降低。运用 SEM、EDAX 和 XRD 研究了镀层的表面形貌和成分。CTAB 分散的纳米 TiO_2-Ni 基镀层表面平整致密、晶粒均匀，镍基晶粒长大伴随着纳米 TiO_2 被夹持嵌埋过程，TiO_2 多分布于镍基间隙。分析认为纳米粉末 TiO_2 与 Ni 符合迁移、吸附、嵌埋的力学共沉积过程。

关键词：电刷镀；表面活性剂；电沉积；涂层特性

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Effect of Surfactants on Electrodeposition of Nano-TiO_2/Ni Composite Coating

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Abstract: The effects of surfactant on the dispersion of nano-TiO_2 and the deposition behavior of nano-TiO_2/Ni composite coating were investigated. Sedimentation experiment was carried out to describe the dispersion effect of nano-TiO_2. The results indicate that cationic surfactant CTAB has better effect on dissipating nano-TiO_2 than other agents, while it will not settle more than 40 minutes, because nano-TiO_2 dispersed uniformly. The microhardness of nano-TiO_2/Ni coating with CTAB is improved largely. Besides, the coating presents great thermal stability and less porosity. CTAB leads to smoother and denser morphology of composite coatings compared with SDBS and PEG. The composite coatings were composed of Ni and TiO_2 based on XRD and EDAX. It is concluded that codeposition behavior of nano-TiO_2 and Ni should be a motion, absorption and mechanics.

Key words: brush plating; surfactants; electrodeposition; mechanic property

0 Introduction

As is all known, producing highly dispersive nano-particle reinforced coatings by using brush plating technique is becoming an active area of research. Brush plating techniques, different from conventional vat plating, are electrochemical process conducteded with an electrolyte applied to the substrate by a so-called brush to form the adherent deposit[1]. Brush plating has been increasingly used in mechanical industry, and more frequently in repairing and maintenance, achieving remarkable economic benefits[1-4]. Unique mechanical properties of nanostructured materials have motivated a worldwide interest to synthesize nanostructured coatings. Thus the application of nanocrystalline materials has diversified into various fields including electrochemical coatings. Brush plating coatings combine the advantages of the brush plating technique (cost effectiveness, simple operation and selective area plating) and the nanostructured coatings[5]. Composite coatings can possess higher hardness levels, wear resistance, self-lubricating characteristics, heat resistance, corrosion resistance and decorative appearance[6].

In previous work, Ni-based composite coatings with nanoparticles, such as Al_2O_3, TiO_2, SiC, ZrO_2, PTFE, and CNTs have been prepared [6-10]. Nano-particles agglomerate to

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form large clusters because of large surface energy. There are some methods used in preparing composite electrobath solutions to ameliorate this effect, such as the addition of metal cationic accelerants and surfactants in the electrobath, the ultrasonic irradiation and the type of applied current[10]. It is a great challenge to prepare highly dispersived reinforced composite coatings for the various particle enforcements.

The objective of this work is to investigate the effect of surfactants on dispersing nano-TiO_2. The codeposition behavior of nano-TiO_2 is discussed based on analyses of microstructure and composition of the composite coatings.

1 Experimental section

Q235 steel discs were used as the cathode, while the anode was a graphite, and it was plated by the special brush plating power of KSD-2000. Before plating, substrates were mechanically polished to 1000-grit finish, then ultrasonically degreased with acetone. Fig. 1 shows a schematic drawing that illustrates the power and different kinds of electrolytes. Nano-TiO_2/Ni coating was prepared according to the procedure: electroclean → activate → Ni preplate → composite bursh plating. It was carried out with a voltage of 12 V and a relative velocity of 6 m/min between the negative and positive pole.

For these series of experiments, nano-TiO_2 particles with a mean diameter of 30 nm (Haitai Nanomaterial Co. Ltd., Nanjing, China) were chosen to codeposit with nickel electric brush solution. The composition of the bath is $NiSO_4 \cdot 7H_2O$(253.0 g/L), $NH_3 \cdot H_2O$(105.0 g/L), $(NH_4)_3C_6H_5O_7$ (56.0 g/L), $(COONH_4)_2 \cdot H_2O$ (0.1 g/L), CH_3COONH_4 (23.0 g/L), meanwhile analytical reagents and deionized water were used in the experiments.

Sedimentation experiment was carried out to compare the dispersion of different surfactants for nano-TiO_2 in the electric brush solution. Five kinds of surfactants (e.g. SDBS, CTAB, PEG400, SDBS + PEG and CTAB + PEG (250 mg/L)) were added with the nanoparticles into the solution accordingly.

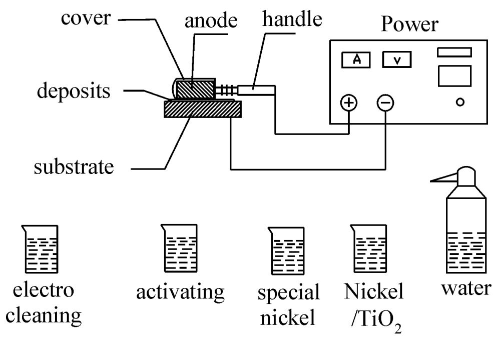


Fig. 1 Schematic drawing of brush plating process

The microhardness of the coatings was measured on HDX-100 hardness tester using a load of 100 g for 15 sec. The surface morphology and microstructure were examined by S-3000N scanning electron microscopy (SEM) and D/Max-3B X-ray diffraction (XRD). The O, Ti and Ni concentration of composite coatings were measured by energy dispersive X-ray analysis (EDAX).

2 Results and discussion

2.1 Effect of surfactants on the dispersion nano-TiO_2

Before brush plating, composite electrobath was stirred sufficiently by high-energy mechanical and ultrasonication method for 0.5 h. Fig. 2 presents the sedimentation time of electrobath with different surfactants. It is clearly observed that electrobath without surfactants addition settles easily, whereas sedimentation time of electrobath with surfactants addition improves significantly. CTAB has better effect on dissipating nano-TiO_2, with sedimentation time up to 40 min. That is to say, the agglomeration of nanoparticles is solved to a certain extent followed by electrobath with anionic surfactant SDBS, which will not form stratification more than 30 min. However, the settling velocity of electrobath with composite surfactants is speeding up evidently compared with anionic surfactant. In addition, dispersing nano-TiO_2 by adding nonionic surfactant PEG is not effective.

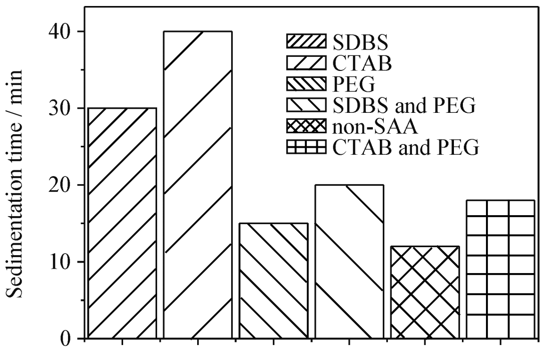


Fig. 2 Effect of adding surfactants on sedimentation time

The main reason of dispersion difference is the adsorption between the nanoparticles surface and electrobath. As a matter of fact, surfactant adsorption forms a monolayer on the nanoparticle surface, and then hinders mutual contacts. With the increasing of the distance among particles, the monolayer reduces the Vander Waals attraction, and stops nano-particles clustering with each others.

2.2 Effect of surfactants on mechanic property

The mechanic property of the composite coating depends on the distribution of nano-TiO_2. Fig. 3 depictes the effect of different surfactants on the microhardness. Microhardness indentations of nano-TiO_2/Ni composite coatings were made into the crosssection to avoid the effect of substrates. It is found that the microhardness of nano-TiO_2/Ni coating dispersed by cationic surfactant CTAB reaches 640 HV, which is much higher than those coatings dispersed by other surfactants. The improvement of microhardness can be explained by the hardening effect of dispersoids (pinning of dislocations and grain boundaries).

Porosity has a significant impact on corrosion resistance of nano-TiO_2/Ni coating in enviroment because corrosive solution generally can permeate into the substrates through these pores. Porosity of composite coating was measured by GB 5935-86. Porosity of nano-TiO_2/Ni coating dispersed by CTAB is only 1.5/cm^2 (Fig. 4), that is to say, uniformly distribution nano-particles makes surface more condensed. On the other hand, SDBS is not effective, with porosity up to 6 /cm^2, which is also more porous than that without surfactant. This is a result of the agglomeration of nanoparticles, forming some small continuous pores.

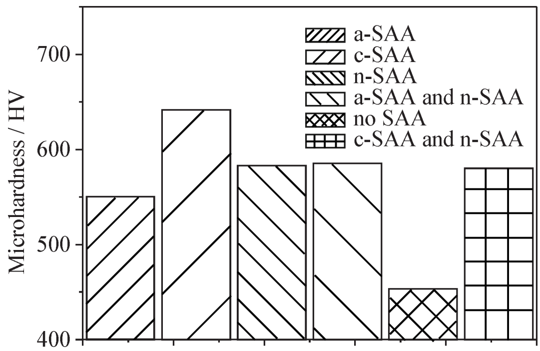


Fig. 3 Effect of adding surfactants on microhardness

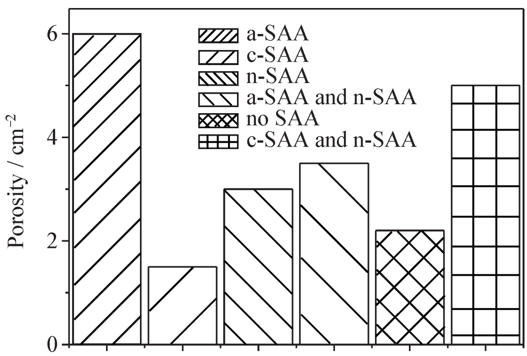


Fig. 4 Effect of adding surfactants on porosity

Thermal microhardness experiments were carried out to compare thermal stability of composite coatings with different surfactants. Fig. 5 shows the microhardness of composite coatings at different temperatures. It can be seen that composite coatings reveal a greater hardness stability in the range of temperature from 100 ℃ to 600 ℃, a dramatic increase was observed while using CTAB. It can be explained that more nano-TiO_2 particles serve as dispersoids in the coating to increase the load-carrying capacity, and in the case of CTAB a more uniform and hence more effective disperdoid of nano-TiO_2.

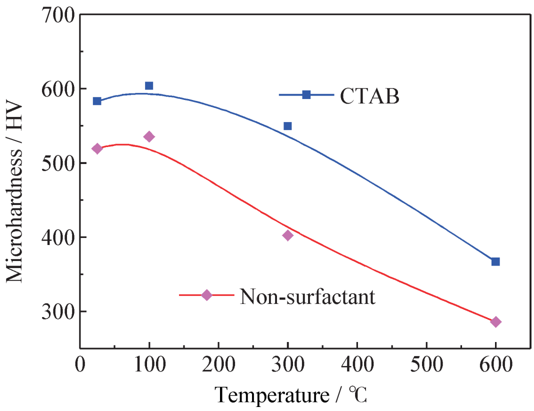


Fig. 5 Thermal stability of composite coatings

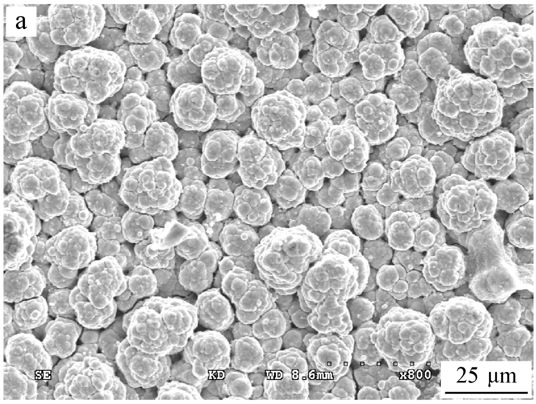
2.3 Effect of surfactants on surface morphology

Fig. 6 demonstrates the effects of adding surfactants on surface morphologies of coatings. Typical cauliflower-like polycrystallites with an average size of 20 μm were formed on the surface of composite coatings owing to point charge effect. The coating with CTAB has the best surface morphology (Fig. 6(a)), which possesses finer, smoother and more compact micro-surface morphology. The next best surface morphology is echibited by the plating with the nonionic surfactant PEG (Fig. 6(b)), while the roughness of the coating with SDBS (Fig. 6(c)) is much higher, which consequently affect the mechanical properties compared as to the properties of the other two surfactants.

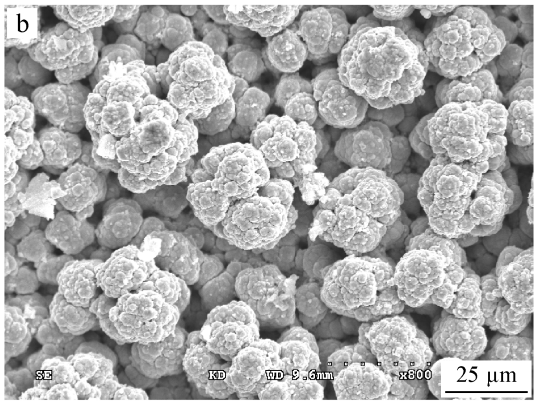
The difference in the efficacy of the various surfactants is due to the positive hydrophilic component of CTAB, adsorbing negative charges of nano-TiO_2 particles in the solution. CTAB reduces the agglomeration of nanoparticles, and provides more Ni nucleation points, making the resuletant coating finer structured and more uniform. Above, it was found that the incorporation of nano-TiO_2 particles in Ni matrix refined the Ni crystal and changed the preferred orientation.

2.4 Microstructure and composition of nano-TiO_2/Ni coating with CTAB

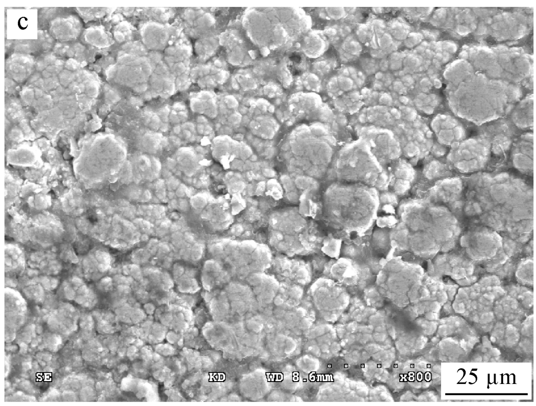
Fig. 7 shows XRD patterns of composite coating with CTAB, which reveals the existence of Ni and TiO_2, with some typical diffraction peaks corresponding to TiO_2 nearly at $2\theta = 27.4°$ and $41.2°$. This is an evidence for the incorporation of more particles in the coating with CTAB. Pure Ni electrodeposited from nickel ions of electric brush solution, whereas the existence of TiO_2 is explained by that nano-TiO_2 is captured, embedded and buried by growing nickel.



(a) CTAB



(b) PEG



(c) SDBS

Fig. 6 Effects of adding surfactants on surface morphology

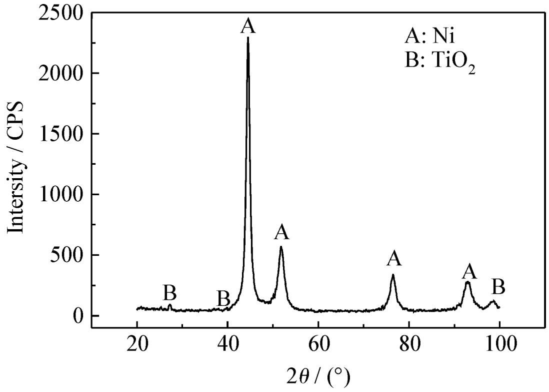


Fig. 7 XRD pattern of composite coatings with CTAB

The concentration of Ti and O was measured to determin the existence of TiO_2 by energy dispersive X-ray analysis. Fig. 8(a) presents the surface morphology of composite coating with CTAB, it was found that TiO_2 codeposited along the boundaries of Ni grains. Fig. 8(b) shows the EDAX spectra of nano-TiO_2/Ni composite coatings with CTAB (Fig. 8(a)). The concentration of element Ti in nano-TiO_2/Ni coating was 3.39%, whereas the element O was 3.12%. It was evidenced that Nano-TiO_2 was distributed homogeneously in the nickel matrix and deposited along electrodeposited Ni grains. EDAX analysis and SEM observation demonstrate that a suitable surfactant plays an important role in determining the microstructure of the composite coatings.

Fig. 9 represents a schematic of the effect on deposition of the nano-TiO_2/Ni coating with CTAB. CTAB makes the steric and electrostatic repulsion of nano-TiO_2 increasing, along with the hydrophilic group adsorbed in the particles surface and hydrophobic group extended into the electrobath. In the deposition process, nano-TiO_2 is agglomerated in the defects of composite coatings, forming a complex ion group with the surfactants and Ni^{2+}, then the complex ion group moved along the direction of electric field force and embedded into plating. On the other hand, nano-TiO_2 is embedded and buried gradually by the growing nickel, while the embeding process depends on the traction of aligned surfactant. In other words, codeposition behavior of nano-TiO_2 and Ni should be a motion, absorption and mechanics mechanism.

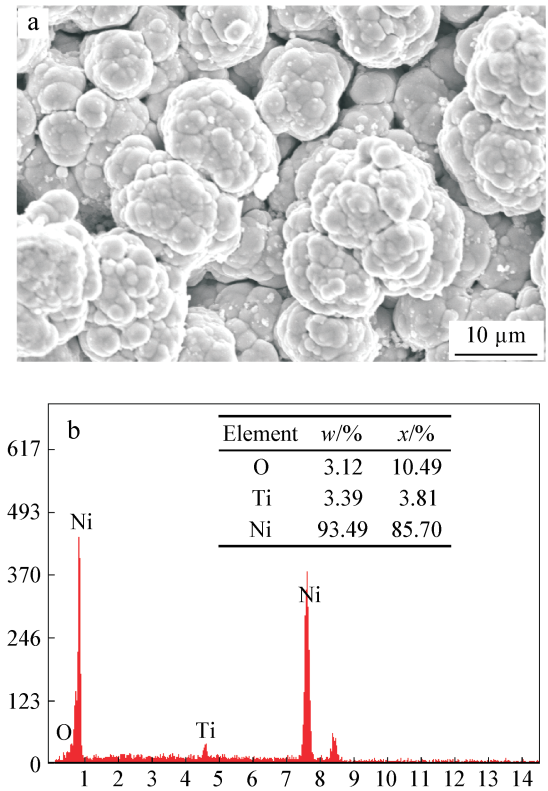


Fig. 8 Microstructure and compostion of nano-TiO_2/Ni composite coatings (a) surface morphology (b) EDAX results

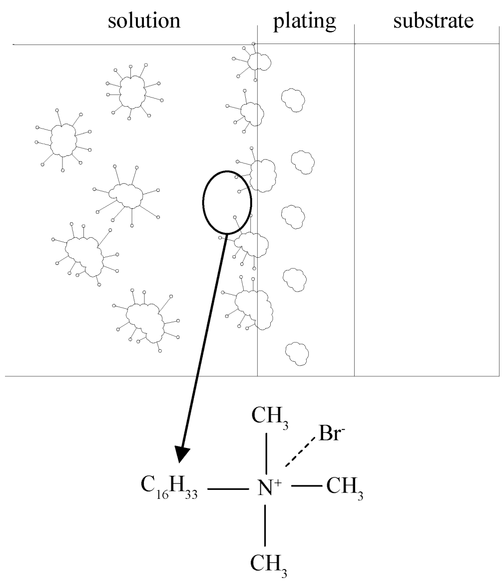


Fig. 9 Schematic of effect on plating deposition with CTAB

3 Conclusions

From the experiments and analyses, the following conclusions are presented. Cationic surfactant CTAB has the best dispersion effect on nano-TiO_2, compared with the other surfactants. It will only form a sediment in more than 40 minutes. Microhardness of nano-TiO_2/Ni composite coatings with CTAB is improved significantly. Additionally, the coating has a greater thermal stability and less porosity owing to a great dispersion of CTAB, which resluts in increasing steric and electrostatic repulsion of nano-TiO_2. The cationic surfactant CTAB leads to fine and smooth morphology. Composite coatings were composed of Ni and TiO_2 based on XRD and EDAX. In short, it is evident that codeposition behavior of nano-TiO_2 and Ni should be a motion, absorption and mechanics mechanism.

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·学术动态·

第六届中国国际摩擦学会议 8 月在兰州召开

8 月 19～22 日，第六届中国国际摩擦学会议在兰州召开，会议以“绿色摩擦学”为主题，由兰州化学物理研究所固体润滑国家重点实验室、清华大学摩擦学国家重点实验室、中国机械工程学会摩擦学分会主办，来自世界 13 个国家的 300 多名摩擦学工作者汇聚一堂，共同研讨近年来摩擦学与润滑技术的最新进展和发展方向。薛群基院士、以色列魏茨曼科学院的 Jacob Klein 教授、英国南安普顿大学的 Robert JK Wood 教授和乔治华盛顿大学的 Stephen M Hsu 做了大会邀请报告。为期 4 天的会议上，各国学者围绕表面与界面、润滑与摩擦化学、材料磨损、纳米和生物摩擦学等主题，从空间摩擦学、润滑基础与技术、材料的疲劳与磨损等 9 个方面展开了充分的交流。 （王文宇 供稿）