

Electrochemical Mechanism and Electroless Plating Characteristics for Surfactants-Assisted Preparation of Cu-Ti₃SiC₂ Coated Powders

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Abstract: To improve the interface bonding strength between copper and ceramics in Cu-(Ti₃SiC₂)_p composites, the Cu-(Ti₃SiC₂)_p coated powders were prepared using environmental friendly ascorbic acid as reducing agent and D-glucose sodium as complexing agent. The electroless copper plating on the surface of Ti₃SiC₂ powder and its electrochemical characteristics were investigated. The modification effects of lauryl sodium sulfate (SDS) combined with polysorbate 80 (Tween-80) surfactants on electroless copper plating were analyzed. Electrochemical mechanism and parameter optimization of this system was predetermined using linear sweep voltammetry and open circuit potential-time method. The results show that the polarization current density can be improved by raising reaction temperature and concentration of Cu (II) and ascorbic acid, which may certainly contribute to accelerate the process of electroless plating. New nuclei are developed from the Ag catalytically activated center implanted on the surface of the copper-coating (Ti₃SiC₂)_p particle, and microspheres with more Ag catalytically active centers promote the formation of copper coatings. Modification effect of combined modifiers of SDS (6~22 g/L) and Tween-80 (8~12 ml/L) is superior to that of single one. The total mole ratio of Cu to Ti₃SiC₂ of the best coating sample is 1:0.54, modified by SM4 (SDS and Tween-80 complex) modifier. Electrostatic effect together with steric hindrance effect play a crucial synergistic role in controlling nuclei and growth of copper on (Ti₃SiC₂)_p surface.

Key words: electroless copper plating; electrochemical characteristics; ascorbic acid; modifiers; (Ti₃SiC₂)_p

Due to excellent thermal and electrical conductivity, (Ti₃SiC₂)_p particle reinforced Cu-(Ti₃SiC₂)_p composites are widely used as electrical brushes, wear-resisting materials, electronic packaging materials, electrical contacts, overhead lines of high speed electrified railways, etc^[1,2]. However, poor interface wettability between copper matrix and reinforcing particles leads to an increase in thermal and electrical contact resistance, which inevitably lowers the thermal and electrical conductivities of Cu-(Ti₃SiC₂)_p composites. Therefore, it is essential to reinforce the interfacial bonding strength between copper and Ti₃SiC₂ powders by improving interfacial microstructure and properties in preparation of composites. Electroless plating copper onto the surface of ceramic

particles is an effective method to overcome this problem^[3-5].

Electroless plating is a self-catalyzed oxidation-reduction reaction, by which metals are deposited onto dielectric surface without external current flow^[4]. In general, hydrazine hydrate, formaldehyde, dimethylamine borane and sodium hydrogen phosphate are used as reducing agents in the electroless copper plating system on ceramic powder surface^[3,4,6-12], and EDTA as chelating agents. However, some of these substances are either carcinogenic or toxic and must be used under alkaline conditions to deposit Cu. Therefore, it is crucial to exploit new non-toxic reducing agents and mixed complexing agents in electroless copper plating^[13-15].

Ascorbic acid (Vc, C₆H₆O₄(OH)₂) as an environmentally

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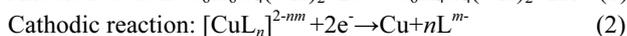
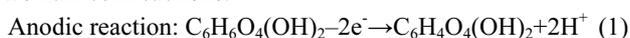
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friendly reducing agent has aroused special attention due to its non-toxic and low cost^[16]. The electrochemical behavior of reaction agents is vital to optimize parameters of electroless copper plating.

However, there are few reports on the electrochemical characterization of this system. So the possibility of using ascorbic acid as reducing agent and CuSO₄ as copper source to coating copper onto Ti₃SiC₂ powders was analyzed through linear sweep voltammetry method (LSV) and open circuit potential-time method (OCPT) in this study. And Cu-coated Ti₃SiC₂ powders were prepared through electroless copper plating method, using lauryl sodium sulfate (SDS) and polysorbate 80 (Tween-80) as modifiers.

1 Experiment

The electroless copper plating system can be described as two half-cell reactions:



where L represents the complexing agent which refers to D-glucose sodium (C₆H₁₁O₇Na); *n* denotes the coordination number; *m* denotes the charge of complexing agent.

1.1 Electrochemical measurement

The electrochemical integrated test system was used. Three-electrode system was chosen to obtain polarization curves: a copper bar ($\Phi 12$ mm) as working electrode, a KCl saturated calomel electrode (SCE) as reference electrode and a platinum/titanium sheet (1 cm×2 cm) as counter electrode.

The working electrode was polished with 1500 mesh waterproof abrasive paper and cleaned with acetone. The solutions were prepared in five-necked flask. The concentration was 0.05–0.2 mol/L for CuSO₄ and 0.05–0.2 mol/L for D-glucose sodium; ascorbic acid was set as 1.5–2 times higher than that of Cu(II). Modifiers were composed of

0–12 g/L SDS and 0–8 ml/L Tween-80. The temperature was controlled in the range of 298–343 K.

The polarization curves were measured using linear sweep voltammetry method, with scanning rates of 0.5 or 1 mV/s. The anodic polarization curves were measured along the positive potential scan direction in Vc-reduced electroless copper plating bath without adding copper ions. The cathodic polarization curves were measured along the negative potential scan direction as well in the same plating bath without adding Vc.

1.2 Pretreatment and electroless copper plating of Ti₃SiC₂ powder

Ti₃SiC₂ powders with an average size of 10 μm were selected as the candidates for coating. The processes of the copper electroless plating are as follows: pretreatment (coarsening and hydrophilization)→surface sensitization and activation treatment→pre-reduction→electroless plating→post process→analysis. The pretreatment step is crucial to attain a good adhesion between copper layer and the surfaces of Ti₃SiC₂ powders.

The pretreatment steps of Ti₃SiC₂ powders are as follows: the selected Ti₃SiC₂ powders are boiled in 20wt% NaOH solution for about 5 min, followed by ultrasonic stirring for 10 min; and then the pretreated samples were coarsened in NaF-HF solution (40 ml/L HF+4 g/L NaF) ultrasonically; after that, the samples were sensitized in SnCl₂-HCl solution (30 g/L SnCl₂·2H₂O+25 ml/L HCl) at 333 K for about 15 min, followed by activating process in AgNO₃-NH₃·H₂O solution (35 g/L AgNO₃+50 ml/L NH₃·H₂O) at 333 K for 10 min.

Subsequently, the pretreated Ti₃SiC₂ powders were pre-reduced by 30 g/L NaH₂PO₂·2H₂O at 343 K for 5 min and then dried in a vacuum drying oven at 333 K for 20–30 h.

To describe the principle of electroless copper plating on (Ti₃SiC₂)_p surface, a schematic diagram is shown in Fig.1. It

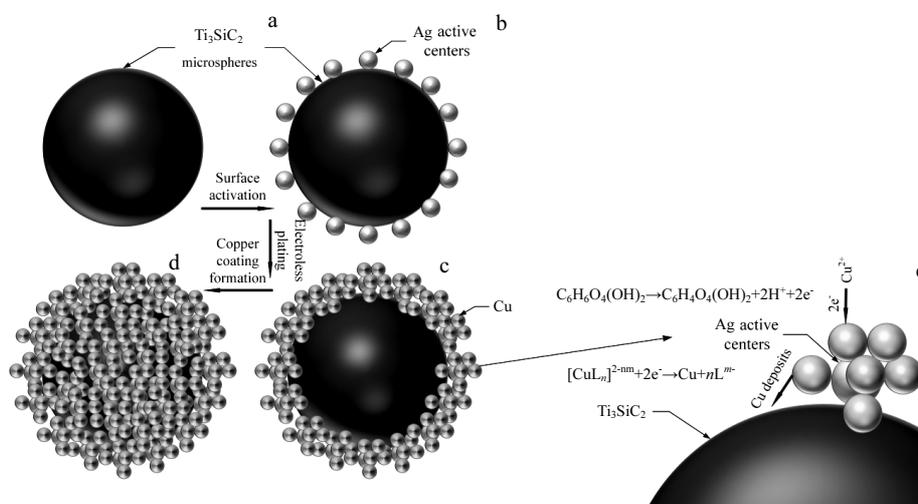


Fig.1 Schematic diagram for electroless copper plating on (Ti₃SiC₂)_p surface: (a) Ti₃SiC₂ microspheres; (b) activated particles; (c) copper nucleation; (d) copper coating formation; (e) partially enlarged drawing

can be seen that newly-born activated Ag particles are deposited onto the Sn sensitized layer, acting as the nucleated center for copper plating on $(\text{Ti}_3\text{SiC}_2)_p$.

The electroless copper plating solutions with differed CuSO_4 contents were prepared. The reducing agents of ascorbic acid, combined with complexing agents and surfactants were dissolved with deionized water in reactor and immersed into water-bath at 333~353 K. And then the pretreated $(\text{Ti}_3\text{SiC}_2)_p$ samples were added into the reactor and stirred at a speed about 200 r/min. In the meanwhile, the prepared CuSO_4 solutions were gradually dropped into the reactor, with a speed of one drop per second, to react slowly with the reducing agent. Brownish-red copper appeared immediately as the CuSO_4 droplets were added. Complexing agents can ensure the gradual progress of the electroless plating process. Well-coated $\text{Cu-Ti}_3\text{SiC}_2$ composites were obtained after reacting for 50~70 min.

1.3 Characterization

The phases of products were identified by X-ray diffraction (XRD, Model Rigaku D/max-2400, Japan). The morphology and element quantitative analysis were conducted using scanning electron microscopy (SEM, Model Supra55 FESEM, ZEISS Germany) and energy-dispersive spectroscopy (EDS, Model Oxford Penta FETx3), respectively.

2 Results and Discussion

2.1 Influence of temperature on the LSV curves

Temperature greatly affects the LSV polarization curves of Cu(II) reduction and $\text{C}_6\text{H}_6\text{O}_4(\text{OH})_2$ oxidation. The cathodic polarization curves with D-glucose sodium containing (shown in Fig.2a) demonstrate that the peak current density is weak at lower temperature. As the temperature increases, the peak current density is enhanced significantly, and $(E_p)_c$ peak slightly offsets to the right. Elevating temperature benefits the Cu(II) reduction reaction, and accordingly accelerates copper deposition rate. It is consistent with the report in Ref.[9].

As shown in Fig.2b, the peak current densities of anodic polarization curves obviously increases as the temperature increases. The maximum current density at 343 K is 30 times larger than at 298 K, which indicates that high temperature promotes the oxidation of ascorbic acid. In the meantime, $(E_p)_a$ peak potential changes to the positive direction because when the temperature rises up, the rate of electrons outflowing from electrode is greater than oxidation rate, which subsequently leads to accumulation of positive charge. As a result, the anode potential seems to shift to the positive side.

2.2 Influence of Cu(II) concentration on the LSV curves

The cathodic polarization curves of copper sulfate were measured at different temperatures. Fig.3 shows the effect of Cu(II) concentration on LSV curves for copper sulfate reduction at 343 K. Polarization current density of cathodic scan is strengthened with the increase of Cu(II) concentration, and polarization potential also deviates negatively. So higher

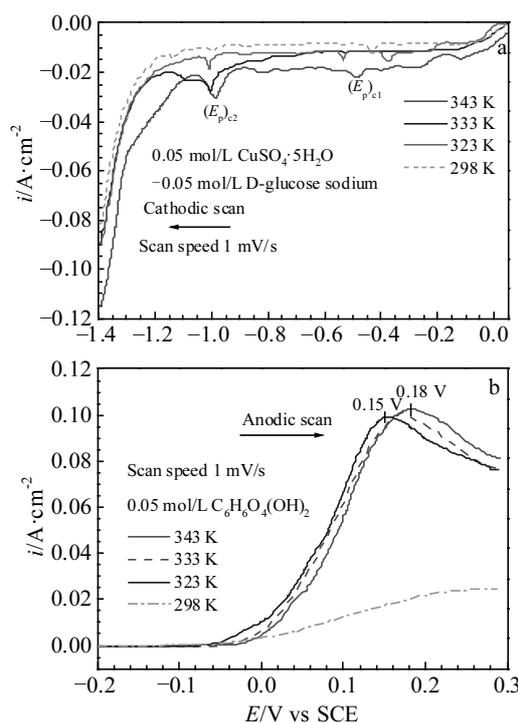


Fig.2 Influence of temperature on the LSV curves of Cu(II) reduction and $\text{C}_6\text{H}_6\text{O}_4(\text{OH})_2$ oxidation: (a) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{D-glucose sodium}$ and (b) $\text{C}_6\text{H}_6\text{O}_4(\text{OH})_2$

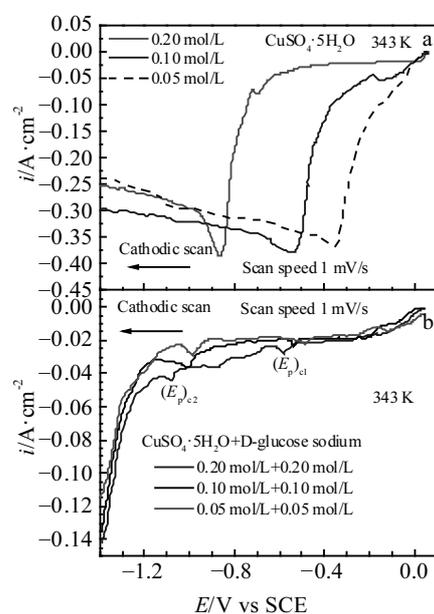


Fig.3 Influence of Cu(II) concentration on LSV curves of copper sulfate reduction at 343 K without (a) and with (b) D-glucose sodium as complexing agent

Cu(II) concentration will conduce to the copper plating. Similar observation has been reported in Ref.[17] using formaldehyde as reductant.

Unlike solution baths without adding complexing agent (Fig.3a), polarization curves of D-glucose sodium baths (Fig.3b) have two reduction peaks. The polarization potential of $(E_p)_{c,1}$ and $(E_p)_{c,2}$ for copper sulfate reduction at 343 K is -0.584 and -1.08 V, respectively. The reason is that by adding D-glucose sodium complexing agent, the copper ions change from Cu(II) hydrated ions to $\text{CuL}_n^{2-n^*m}$ complex ion. As a result, it leads to fewer amounts of free Cu(II) ions and low electronic transmission speed. Consequently, reduction rate decreases significantly because of a relatively slow deposition precipitation.

2.3 Influence of V_c concentration on the LSV curves

Fig.4 shows the influence of $\text{C}_6\text{H}_6\text{O}_4(\text{OH})_2$ concentration on the LSV curves of anodic polarization. Without adding $\text{C}_6\text{H}_6\text{O}_4(\text{OH})_2$, the weak $(E_p)_a$ peak appears at about 0 V at 323 K, which corresponds to the Cu(I) formation^[18]. Another $(E_p)_a$ peak, nearly 0.181 V, associates with the oxidation reaction of Cu and Cu(I). This phenomenon is similar to the report of the formaldehyde-EDTA system where a slight positive deviation of $(E_p)_a$ is found^[17].

With the increase of ascorbic acid, current density is enhanced significantly, and the peak potential shifts negatively. The lowest anode polarization potential is 0.116 V. It indicates that increasing the concentration of ascorbic acid can promote self-oxidation. The results of anodic polarization at 343 K are similar to that at 323 K, but the current density and the corresponding potential change slightly in the positive direction.

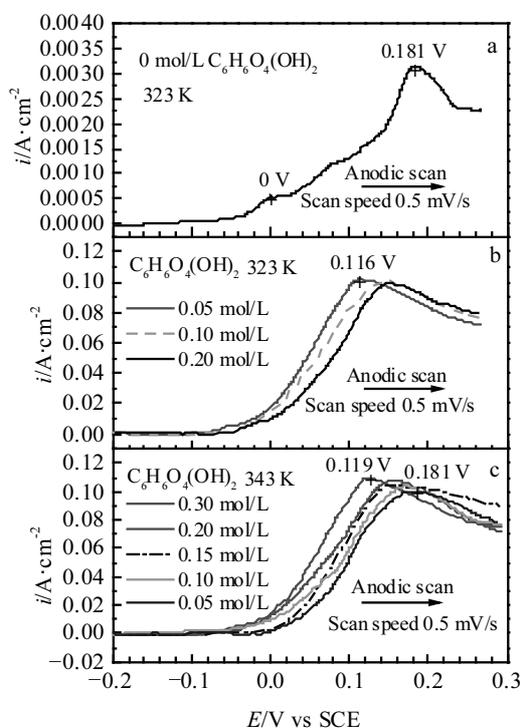


Fig.4 Influence of $\text{C}_6\text{H}_6\text{O}_4(\text{OH})_2$ concentration on LSV curves: (a) without $\text{C}_6\text{H}_6\text{O}_4(\text{OH})_2$, 323 K; (b) $\text{C}_6\text{H}_6\text{O}_4(\text{OH})_2$, 323 K; (c) $\text{C}_6\text{H}_6\text{O}_4(\text{OH})_2$, 343 K

So it is suitable to set the concentration of $\text{C}_6\text{H}_6\text{O}_4(\text{OH})_2$ at about 1.5~2 times the concentration of Cu(II).

2.4 Influence of temperature and concentrations on OCPT curves

Mixed open circuit potential-time (OCPT) curves shown in Fig.5 are also used to judge the possibility of ascorbic acid reducing copper plating process. When the plating bath temperature reaches to 343 K, the first mixed potential step appears at -30 mV within 100 s, and then increases immediately, approaching 42 mV in 480 s. The solution color rapidly turns to red after 100 s and fine copper coated particles are generated. The pH value of solution shifts to about 0.6. According to the mixed potential-time results, it can be deduced that chemical plating process is triggered at 323 K and accelerated sharply at 343 K. Combined with Fig.5b, it can be known that as the temperature and concentrations of mixed solution increase, the oxidation-reduction reaction is promoted rapidly.

2.5 Effect of surfactants on electroless copper plating

Experiments of electroless copper plating on $(\text{Ti}_3\text{SiC}_2)_p$ surface with different surfactants were conducted at 343 and 353 K. It is discovered that the optimum temperature for obtaining the best copper deposition rate and XRD phase characterization is 353 K^[19]. The composition of modifiers and modification effects using mixed modifier are shown in Table 1. It can be seen that the modification effect of SM3~SM5,

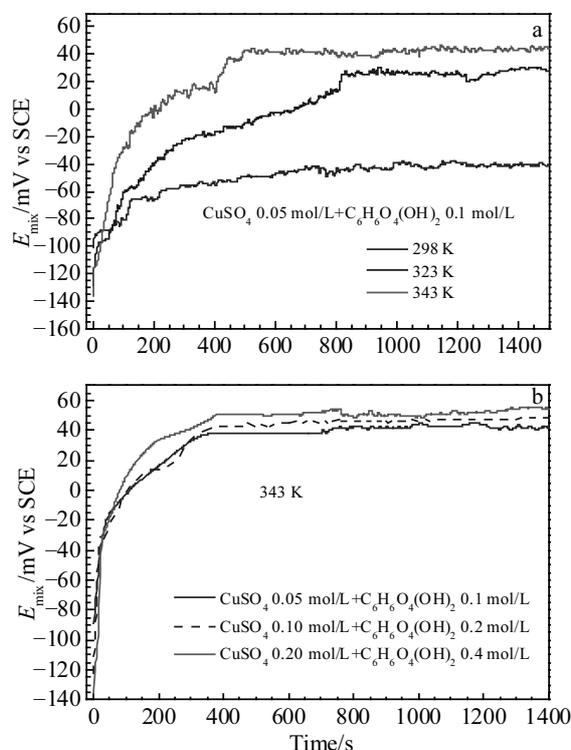


Fig.5 Mixed potential-time curves for mixed plating liquids at different temperatures (a) and concentrations (b)

Table 1 Composition of modifiers and modification effects

Sample	Composition	System condition	Coating effect
SM1	20ml/L Tween-80	Well dispersed, deposit slowly	Incompletely coated, dendritic growth
SM2	2 g/L SDS+18 mL/L Tween80	Well dispersed, deposit slowly	Incompletely coated, dendritic growth
SM3	6 g/L SDS +14 mL/L Tween80	Well dispersed, deposit fast	Well-coated, near-spherical
SM4	10 g/L SDS+10 mL/L Tween80	Well dispersed, deposit fast	Well-coated, near-spherical
SM5	12 g/L SDS+8 mL/L Tween80	Well dispersed, deposit fast	Well-coated, near-spherical
SM6	18 g/L SDS+2 mL/L Tween80	Well dispersed, deposit slowly	General coated, dendritic crystalline
SM7	20 g/L SDS	Well dispersed, deposit slowly	Incompletely coated, dendritic growth
SM8	18 g/L SDS+12 mL/L Tween80	Well dispersed, deposit slowly	Well-coated, near-spherical
SM9	22 g/L SDS +8 mL/L Tween80	Well dispersed, deposit slowly	Well-coated, near-spherical

SM8 and SM9, which have well-coated $(\text{Ti}_3\text{SiC}_2)_p$ near-spherical copper crystals, is better than that of SM1, SM2, SM6 and SM7.

The SEM micrographs and EDS analysis results of copper-coated Ti_3SiC_2 powders modified by different modifier are shown in Fig.6~Fig.8. It can be seen that well-coated $\text{Cu}-(\text{Ti}_3\text{SiC}_2)_p$, in which copper particles grow from the Ag activated nuclei on Ti_3SiC_2 surface, is obtained under proper process conditions modified by SM3, SM4, SM5, SM8 and SM9 combined with surfactants. The SEM micrograph and EDS results of powders modified by SM4 clearly demonstrate that copper crystal is wholly coated on the surface of Ti_3SiC_2 particles, and copper particles are instinctively deposited (Fig.6). The surface layer is composed of 23.04at% Cu, 36.77at% Ti, 12.42at% Si and 25.43at% C, based on EDS analysis with a total mole ratio of Cu to Ti_3SiC_2 of 1:0.54. It indicates that the $(\text{Ti}_3\text{SiC}_2)_p$ particles are almost coated by copper. From the EDS results and surface element mapping in

Fig.6, it can be seen that the element distribution of Ti, Si and C atom in the selected area is very uniform, matching well with the stoichiometric ratio of Ti_3SiC_2 . The detected Ag on the surface comes from the sensitization and activation treatment. These Ag particles are expected to act as the activative center for Cu(II) reduction^[4,20].

Similar good coating effect is also found for SM5 (shown in Fig.7), SM8 and SM9 (not shown here), but incomplete coating is observed for SM1 (shown in Fig.8), SM2, SM6 and SM7 (not shown here). Under high magnification, new copper crystal precipitates can be found clearly on the surface of the Ti_3SiC_2 modified by SM5 (Fig.7). EDS element mapping shows that this particle is rich-in Cu but depleted in Ti, Si and C, suggesting that it is a copper precipitate. An observation of the very rough surface of this precipitate also suggests the formation of coating layer. However, the copper coating effects of SM1 and SM2 modified samples are poor (as shown in Fig.8). To understand this, the mechanisms of different

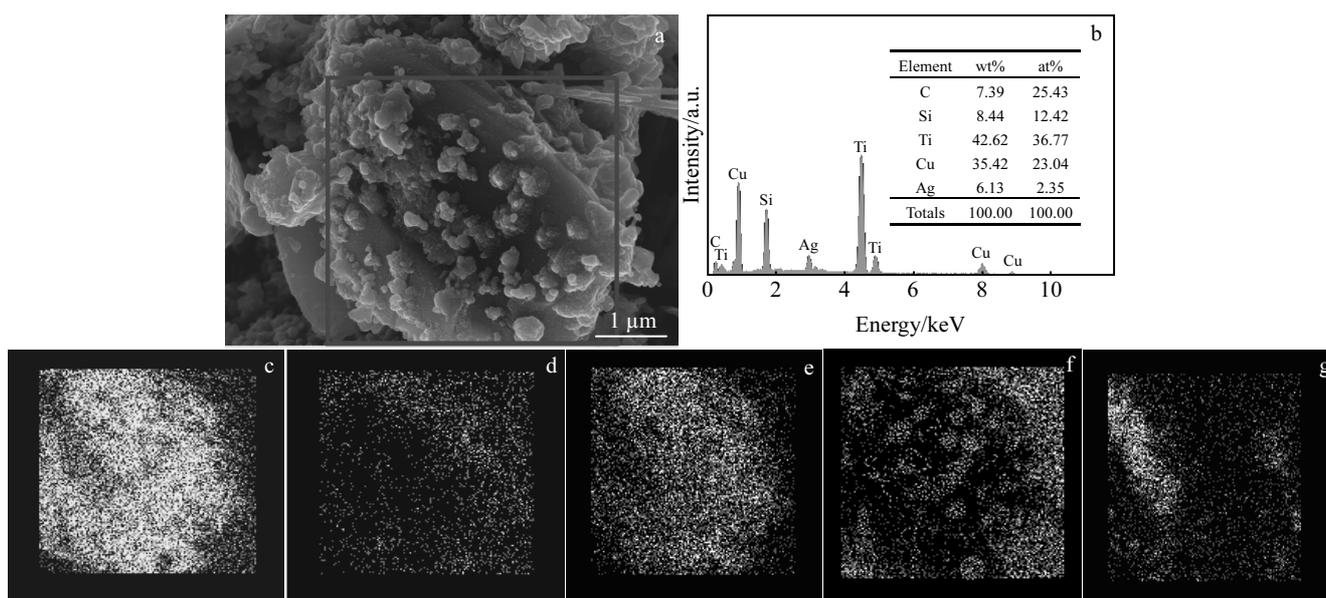


Fig.6 SEM micrograph (a), EDS results (b) and element mapping of Ti (c), C (d), Si (e), Cu (f) and Ag (g) for copper-coated Ti_3SiC_2 powders modified by SM4 surfactant at 353 K

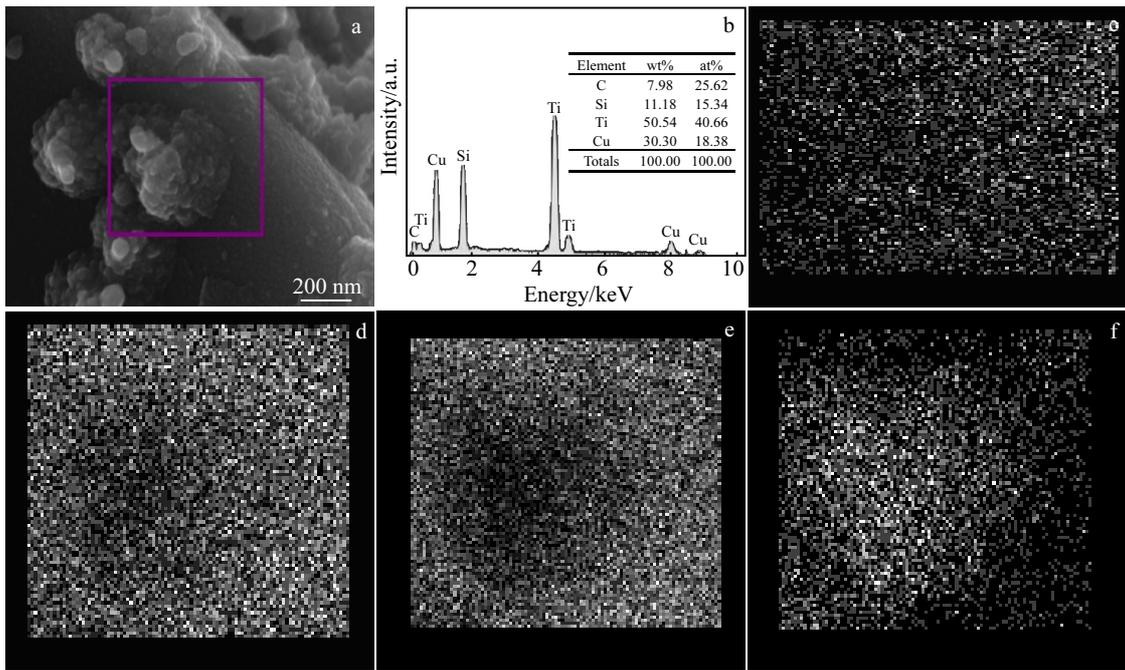


Fig.7 SEM micrograph (a), EDS results (b) and element mapping for C (c), Si (d), Ti (e) and Cu (f) for copper-coated Ti_3SiC_2 powders modified by SM5 surfactant

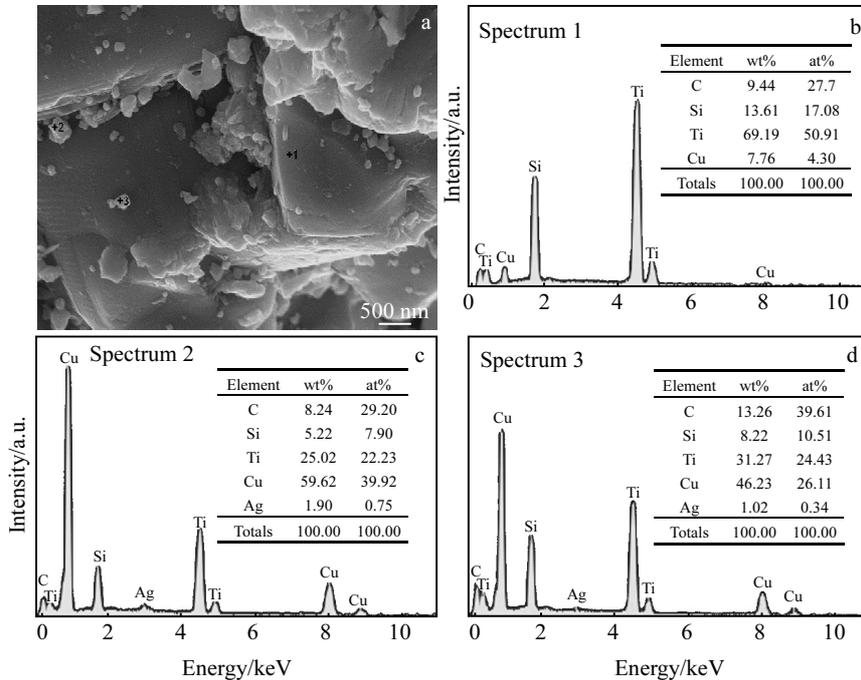


Fig.8 SEM micrograph (a) and EDS results (b-d) of copper-coated Ti_3SiC_2 powders modified by SM1 surfactant

modifiers must be analyzed.

The dual effects of electrostatic attraction and steric hindrance of the modifiers are the decisive factor, and the activated crystal nucleus of Ag contributes to obtain uniform

growth of copper layer. Due to the electrostatic attraction of heterogeneous electric field for $-SO_3$ groups in SDS compounds, the Cu(II) can be adsorbed to the surface of the Ag activated crystal nucleus of $(Ti_3SiC_2)_p$, and then deposited

in-situ. In addition, enhanced stereo-hindrance effects of macromolecule chain of Tween-80 are benefit to uniform copper deposition. Therefore, by adjusting the concentration of modifiers close to critical micelle concentration (CMC), like SM4, SM5, SM8 and SM9, well-coated Ti_3SiC_2 samples with uniform copper layer are obtained because of the synergistic effects of stereo-hindrance and electrostatic effect of modifiers.

3 Conclusions

1) The polarization current density of copper sulfate solution is improved as the Cu(II) and $\text{C}_6\text{H}_6\text{O}_4(\text{OH})_2$ concentration and temperature increase, which is conducive to the oxidation of ascorbic acid. Adding D-glucose sodium as a complexing agent, the LSV polarization curves have two reduction peaks, $(E_p)_{c,1}$ and $(E_p)_{c,2}$ potentials are -0.4 V to -0.6 V and -0.9 V to -1.1 V , respectively. Complexing agents can insure that the reaction is slowed down to uniform the reduction and deposition of copper.

2) Copper particles grow along the Ag catalytically activated nuclei on Ti_3SiC_2 surface to obtain well-coated $\text{Cu}/(\text{Ti}_3\text{SiC}_2)_p$ modified by complex surfactants of SDS and Tween-80. The best coated sample modified by SM4 has a total mole ratio of Cu to Ti_3SiC_2 of 1:0.54. Synergistic effect of electrostatic attraction from SDS and stereo-hindrance from Tween-80 is considered as the critical factor controlling the uniformity of crystal nuclei and growth of copper on the ceramic surface.

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表面活性剂辅助制备 $\text{Cu-Ti}_3\text{SiC}_2$ 包覆粉末的电化学机理和化学镀特性

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摘要: 为提高 $\text{Cu-(Ti}_3\text{SiC}_2)_p$ 复合材料中铜与陶瓷的界面结合强度, 以环境友好型抗坏血酸为还原剂, D-葡萄糖酸钠为络合剂, 制备了 $\text{Cu-Ti}_3\text{SiC}_2$ 包覆粉末。研究了 Ti_3SiC_2 粉末表面化学镀铜及其电化学性能, 以及十二烷基硫酸钠(SDS)结合聚山梨酯 80(Tween-80)表面活性剂对化学镀铜的改性效果。采用线性扫描伏安法和开路电位-时间法确定了该体系的电化学机理并进行参数优化。结果表明, 提高反应温度, 增加 Cu(II) 和抗坏血酸的浓度, 可以提高极化电流密度, 有利于加速化学镀。铜镀层新核从依附在 $(\text{Ti}_3\text{SiC}_2)_p$ 粒子表面的银催化活化中心开始形成, 表面具有较多 Ag 催化活性中心的微球会促进涂层的形成。采用复配改性剂 SDS (6-22 g/L) + Tween-80 (8-12 mL/L) 对化学镀铜表面涂覆的效果优于单一改性剂。采用 SM4 (SDS+Tween-80)改性剂达到最佳涂层效果的 Cu 与 Ti_3SiC_2 的总摩尔比为 1:0.54。静电效应和空间位阻效应对铜在 $(\text{Ti}_3\text{SiC}_2)_p$ 表面的生长起着至关重要的协同控制作用。

关键词: 化学镀铜; 电化学特征; 抗坏血酸; 改性剂; $(\text{Ti}_3\text{SiC}_2)_p$

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