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Improving adhesion strength of sol-gel coating on CoCrMo by electrochemical pretreatment

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Abstract

Keywords: Sol-gel coating; CoCrMo alloy; Electrodeposition; Electro-etching; Scratch test

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1. Introduction

2. Materials and methods

2.1. Pre-treatment of CoCrMo substrate

CoCrMo alloy (composition in wt.%: 64.2% Co, 28.8% Cr, 6.0% Mo, with minute amounts of Si, Mn, C and trace amounts of Ni and Fe, conforming to ASTM F75) was cut into plates of dimensions 15 mm × 15 mm × 2 mm. The CoCrMo plates were polished with sandpaper from #360 down to #2000 and finally with polishing paste (1 μm). Polished CoCrMo plates were treated by electro-etching and electrodeposition, respectively, as show in Fig. 1. Sulfuric acid (H_2SO_4) solution at pH of 2 was employed as electro-etching solution. A solution containing 0.02M $CoSO_4$ at a pH value of 2 (adjusted using H_2SO_4) was used as Co source in electrodeposition of Co on the CoCrMo substrates. The electrochemical parameters applied in the experiment of electro-etching, and electrodeposition are presented in Table 1.

Table 1

Parameters of electro-etching and electrodeposition.

	Electro-etching-1	Electro-etching-2	Electrodeposition-1	Electrodeposition-2
Current density (mA/cm^2)	25	50	-100*	-200*
Time (s)	100	150	150	200

*a negative value indicates current being towards the substrate, which is the cathode.

2.2. Preparation of ZrO_2 sol-gel coatings on pretreated CoCrMo

Before the addition of precursor zirconium (IV) n-propoxide ($Zr(OPr)_4$) (70%wt. in 1-proponal, Aldrich corporation), deionized water (H_2O), magnesium acetate tetra-hydrate (MgAc) and acetylacetone (AcAc) were added into 1-proponal to avoid

premature formation of $Zr(OPr)_4$. In this work, the molar ratio of $Zr(OPr)_4$:H_2O:PrOH:AcAc:MgAc was set as 1:5:20:0.8:0.11 according to our previous work [1]. The solution was stirred for 30 min to get a clear and homogenous solution. After 3 h of aging at room temperature, the precursor solution was used to prepare Mg-stabilized ZrO_2 sol-gel coatings on the pretreated CoCrMo substrate using a dip-coating machine (PTL-MM01, MTI corporation) with a speed of 10 cm/min. Then after sintering at 500°C [1], ZrO_2 sol-gel coatings were formed on the substrate. Coated samples with different pre-treatments were designated as ZrO@CoCrMo, ZrO@Etch1, ZrO@Etch2, ZrO@Electro1 and ZrO@Electro2, as shown in Fig. 1.

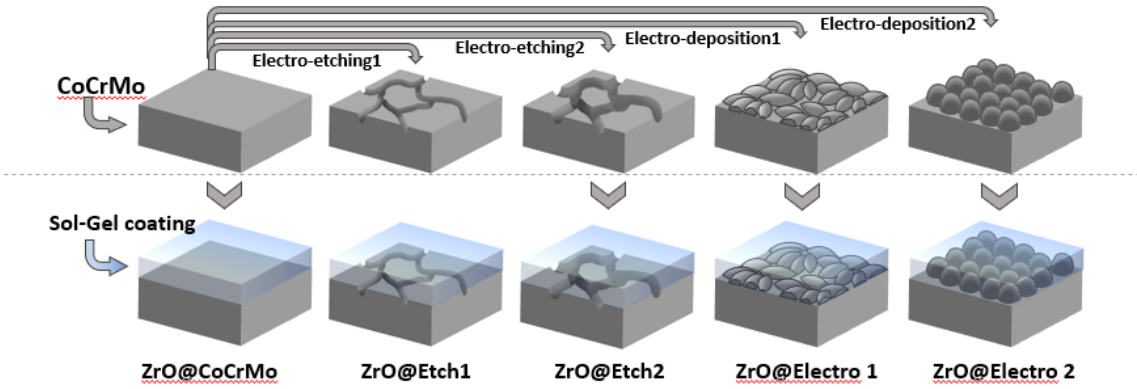

Fig. 1. Diagram showing different preparation routes.

2.3. Microstructural characterization

The surface morphology of different samples was investigated using scanning-electron microscope (SEM, Tescan Vega3). The phase compositions were studied by X-ray diffractometry (XRD, Rigaku smartLab) with Cu Ka ((λ=0.15405 nm) at a scanning rate of 2°/min.

2.4 Scratch test

Scratch test was conducted to semi-quantitatively evaluate the adhesion strengths of ZrO_2 sol-gel coatings on different pretreated CoCrMo substrates [1]. A scratch test machine equipped a Rockwell C diamond indenter with a 200-μm radius tip was used to conduct the scratch test, and the applied load increased from 0 N to 25 N during the test. Critical loads including the load of first crack (Lc1) and the load of breakthrough (Lc2) [2][3] were introduced to evaluate the adhesion properties of different sol-gel coatings. After the scratch test, scratch tracks on the surface of different samples were captured by a reflected-light optical microscope (OM, Leica DM4000M).

3. Results and discussion

Fig. 2 shows the SEM surface morphology of CoCrMo plates after polishing, electro-etching 1, electro-etching 2, electrodeposition 1 and electrodeposition 2, respectively. The surface after mechanical polishing has the lowest roughness (Fig. 2(a)). After electro-etching, crevices were formed at the grain boundaries and most of the second phases were removed as shown in Fig. 2 (b) and (c). Fig. 2(d) shows the surface morphology of CoCrMo after electrodeposition 1, which consists of flakes with a thickness of several hundred nm. Compared with electrodeposition 1, electrodeposition 2 has higher surface roughness and its morphology changes from flake-like to particle-like (Fig. 2(e)).

Fig. 3 shows the SEM morphology of sol-gel coated samples: ZrO@CoCrMo, ZrO@Etch1, ZrO@Etch2, ZrO@Electro1 and ZrO@Elecro2, respectively. Compared with other samples, ZrO@CoCrMo and ZrO@Electro1 are obviously smoother and without obvious cracks. Because the crevices in the boundaries resulted in the stress concentration of ZrO_2 sol-gel coating, some fine cracks formed on the coating above the

grain boundaries of sample ZrO@Etch1. While the crevices formed on the substrate of ZrO@Etch2 are larger than that of ZrO@Etch1, obvious cracks formed on the surface of sample ZrO@Etch2.

Backscattered electron (BSE) cross-sectional images were captured to get the contrast of sol-gel coating. Fig. 4 shows the cross-section of different samples. As the arrows indicate in Fig. 4, the thickness of all ZrO_2 sol-gel coatings is about 500 nm. The Co electrodeposited films are shown by the dashed lines in Fig. 4 (d) and (e). It is obvious that, the Co film on ZrO@Elecro2 (about 500 nm) is obviously thicker than the film on ZrO@Elecro1 (about 200 nm).

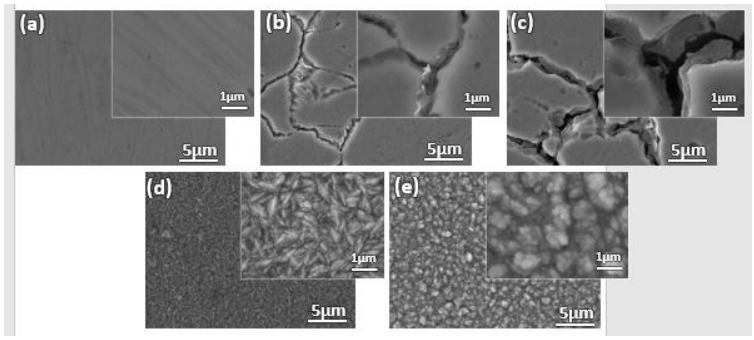

Fig. 2. SEM surface morphologies of CoCrMo after (a) polishing, (b) electro-etching1, (c) electro-etching2, (c) electro-deposition1 and (d) electro-deposition2.

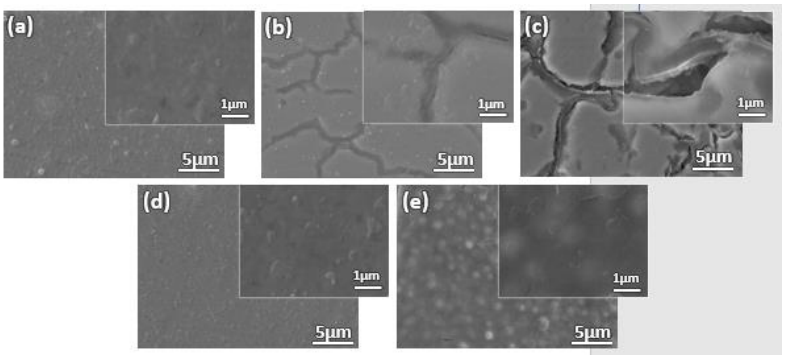

Fig. 3. SEM surface morphologies of sol-gel coated samples: (a) ZrO@CoCrMo, (b) ZrO@Etch1, (c) ZrO@Etch2, (d) ZrO@ Electro1 and (e) ZrO@ Electro2.

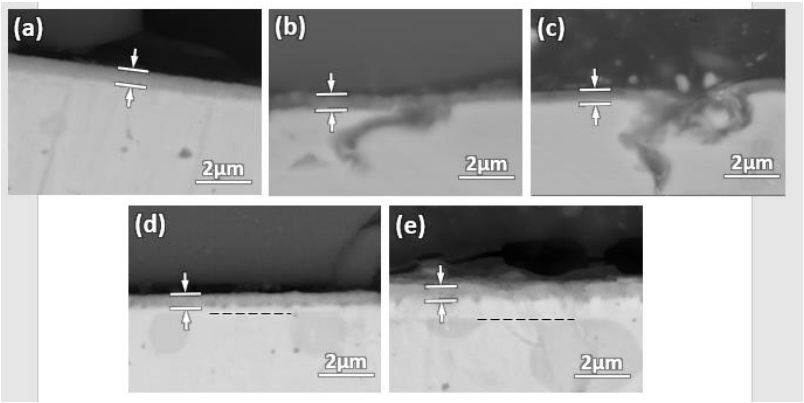

Fig. 4. BSE cross-section morphologies of samples: (a) ZrO@CoCrMo, (b) ZrO@Etch1, (c) ZrO@Etch2, (d) ZrO@ Electro1 and (e) ZrO@ Electro2.

Fig. 5 shows the XRD patterns of CoCrMo and so-gel coatings prepared on pretreated CoCrMo substrates. The XRD patterns of CoCrMo substrate shows typical peaks of CoCrMo which consists of HCP and FCC phase [4]. All samples with sol-gel coating have the peak of tetragonal ZrO_2 (t- ZrO_2) at $2\theta = 30.2$ corresponding to the lattice plane of (111) [5]. Compared with the other samples, the intensities of peaks at $2\theta = 46.8$ in the patterns of sample ZrO@Etch1 and ZrO@Etch2 are obviously lower, which may be caused by the dissolution at grain boundaries. Two low peaks at about $2\theta = 44.4$ and 76.1 appear in the patterns of ZrO@ Electro1 and ZrO@ Electro2, which correspond to the diffraction peaks of electrodeposited Co.

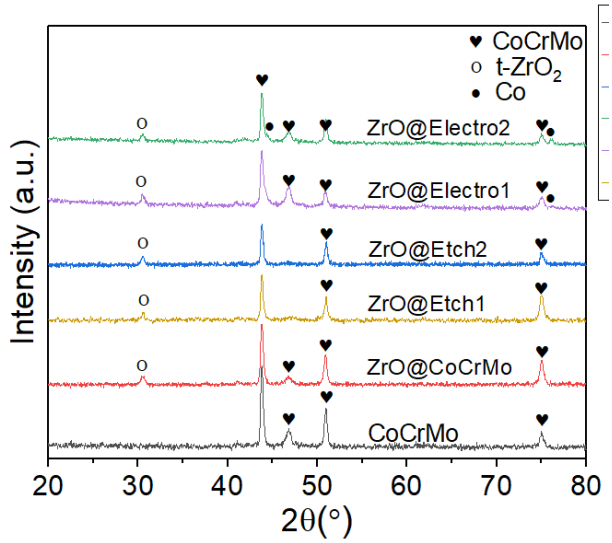

Fig. 5. XRD patterns of CoCrMo and ZrO_2 sol-gel coatings on pretreated CoCrMo.

The scratch test tracks are presented in Fig. 6. Corresponding critical loads (Lc1 (white arrow) and Lc2 (black arrow)) are presented in Table 2. It should be noted that it is difficult to determine Lc1 in some cases (Fig. 6(b) and (c)).

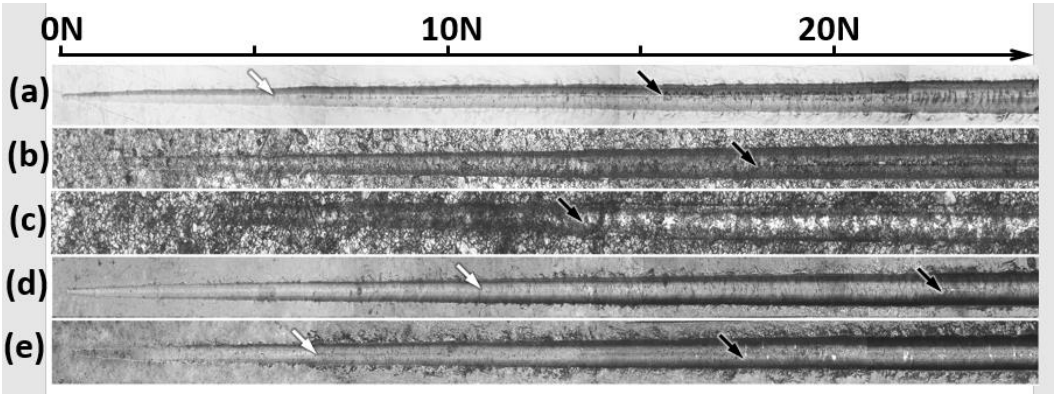

Fig. 6. Optical images of scratch tracks of coated samples: (a) ZrO@CoCrMo, (b) ZrO@Etch1, (c) ZrO@Etch2, (d) ZrO@Electro1 and (e) ZrO@Electro2.

Table 2

Critical loads in scratch test shown in Fig. 6.

Sample	ZrO@CoCrMo	ZrO@Etch1	ZrO@Etch2	ZrO@Electro1	ZrO@Electro2
Lc1 (N)	~6	---	---	~11	~7
Lc2 (N)	~16	~18	~14	~22	~17

4. Conclusions

Mg stabilized t-ZrO_2 sol-gel coatings were prepared on different pretreated CoCrMo substrates. Appropriate electro-etching and electro-deposition can improve the adhesion property of the ZrO_2 sol-gel coating on CoCrMo alloy substrate.

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