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Effects of Sintering Temperature on Structural, Morphological, and Mechanical Properties of Co-Cr-Mo Alloys Coated with ZrO_2 Ceramic Films

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In this study, ZrO_2 thin films were coated on Co-Cr-Mo alloys by screen printing and spraying, which was followed by sintering at a high temperature of 750, 900, or 1100 °C to enhance the characteristics of the coated alloys. Through X-ray diffraction (XRD) measurements, scanning electron microscopy (SEM), surface roughness measurements, and microscale hardness testing, the structural, morphological, and mechanical characteristics of the Co-Cr-Mo alloys coated with ZrO_2 films were investigated in detail. The experimental results revealed that both the microhardness and smoothness of the ZrO_2 ceramic films prepared by screen printing and spraying methods clearly improved with increasing sintering temperature. It was also found that the increase in the sintering temperature contributes to the increased thickness and density of the films, leading to enhanced mechanical properties of the Co-Cr-Mo alloys. After sintering at 1100 °C, the ZrO_2 film prepared by spraying had the smoothest surface (surface roughness: 0.70 μm) and the highest hardness (767 $HV_{0.5}$). The results confirm that ZrO_2 coatings on Co-Cr-Mo alloys have high potential for medical implant applications. In addition, the sintering process is helpful for improving the mechanical properties. The ZrO_2 materials are used in many sensor applications, and sensing applications can be realized using ZrO_2/Co-Cr-Mo materials. In the future, we will study the sensing performance of ZrO_2 sensors fabricated on Co-Cr-Mo alloys as well as implants made of the coated alloys.

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1. Introduction

In recent years, Co-Cr-Mo alloys have been widely used for medical implant applications including the replacements of human joints (hip joint and knee) and dental treatments.(1–3) In particular, as dental applications, Co-Cr-Mo alloys are practically applied in the base plates in complete dentures, bridgeworks, and dental implants. This is because of the many advantages of Co-Cr-Mo alloys, including good mechanical properties, excellent wear resistance, superior corrosion resistance, and extremely high biocompatibility with the human body. It is well known that the high biocompatibility of Co-Cr-Mo alloys is correlated with their superior corrosion resistance. As Co-Cr-Mo alloys are manufactured, a very thin passive oxide film composed of Cr_2O_3 is formed spontaneously on their surface, resulting in their excellent corrosion resistance. Although the passive oxide film generated on the surface of Co-Cr-Mo alloys can suppress the dissolution of metal ions, when Co-Cr-Mo alloys are immersed in various solutions and biological environments, the Co element is easily dissolved. This will result in the instability of the oxide film in the human body. Despite the many advantages of Co-Cr-Mo alloys given above, the release of metal elements from orthopedic implants into body fluids is unavoidable. The metal elements released from Co-Cr-Mo alloys accumulate at the interface between the body tissue and the implant. Then, they migrate through the tissue, which is very detrimental to the human body.

To overcome these disadvantages of applying Co-Cr-Mo materials in implants, it is advantageous to coat them with a ceramic film.(4–6) Many ceramic films, including TiN, TiC, and ZrO_2, have been deposited on the surface of Co-Cr-Mo alloys.(7–9) Because of its biocompatibility and bioactivity, ZrO_2 is one of the most promising ceramic materials for biomedical applications. In addition, ZrO_2 also possesses excellent chemical stability and high hardness, resulting in good protective properties. Moreover, ZrO_2 materials are also used in many sensing applications such as chemical sensors and gas sensors. As well as medical applications, Co-Cr-Mo alloys have also been applied in engineering, such as aero engine gas turbines, and biomedical engineering. Through the deposition of ZrO_2 films on Co-Cr-Mo, its functionality is expected to be increased. ZrO_2 ceramic films have been prepared on Co-Cr-Mo alloys by various techniques including plasma spraying, electrolytic coating, and sol-gel spin coating. To further enhance the mechanical characteristics of ZrO_2 films, sintering processes have usually been used. Nevertheless, up to now, there has been almost no research on the deposition of ZrO_2 films on Co-Cr-Mo alloys by sintering to improve their mechanical characteristics.

In this study, to expand the biomedical applications of Co-Cr-Mo alloys and enhance their mechanical properties, the ZrO_2 coating and sintering techniques were both used. Two coating methods, i.e., spraying and screen printing, were employed to deposit ZrO_2 ceramic films on Co-Cr-Mo alloys. Then, the samples were sintered in a thermostatic furnace at 750, 900, and 1100 °C. The effects of the coating method and sintering temperature on the surface morphology, crystal structure, and mechanical properties of the ZrO_2 coatings on Co-Cr-Mo implant alloys were investigated in detail from the viewpoint of their future application as sensing and implant materials.

2. Experimental Method

In our work, the substrates employed for the ZrO_2 growth were Co-Cr-Mo (ASTM F1537, ASTM F799) standard forging alloys for surgical implants. The composition of the Co-Cr-Mo alloy was C (0.04%), Mn (0.81%), Si (0.16%), Cr (27.58%), Ni (0.14%), Mo (5.48%), Co (64.99%), and N (0.16%). The disc-shaped Co-Cr-Mo alloy samples had a diameter of 31.75 mm and a thickness of 6 mm. To obtain a low surface roughness (R_a), the Co-Cr-Mo samples were polished with sandpaper and diamond paste in sequence. Before the ZrO_2 coating process, the samples were ultrasonically cleaned in acetone and isopropyl alcohol to remove organics and other impurities. The ZrO_2 slurry used for spraying and screen printing was prepared by grinding ZrO_2 ceramic powder, then mixing it well in a solution containing Y_2O_3 powder, a dispersant, and an adhesive (or thickener) to form the ZrO_2 slurry.

As mentioned above, spraying and screen printing methods were both used for coating the ZrO_2 on the Co-Cr-Mo alloy. During the spraying process, the ZrO_2 slurry was spurted from a spray gun and coated on the Co-Cr-Mo alloy 20 times. On the other hand, both the same strength (squeegee pressure: 2 kgw) and the same printing direction were used for ZrO_2 coatings on Co-Cr-Mo alloys in the screen printing technique. After coating the ZrO_2 layer, the sample was subsequently placed in a high-temperature furnace to perform the sintering experiments. Three sintering temperatures, 750, 900, and 1100 °C, were set for these samples and the sintering time was fixed at 1 h. In addition, the heating and cooling rates for the sintering process were fixed at 240 and 60 °C/h, respectively.

The crystal structures of the ZrO_2-coated Co-Cr-Mo samples were determined by X-ray diffraction (XRD) (PANalytical, X'Pert Pro MRD). In the XRD measurement, the Cu Kα line ($\lambda = 1.541874$ Å) was employed as the source and Ge (220) was adopted as the monochromator. The surface morphologies of samples were observed by scanning electron microscopy (SEM) (S-3000H, Hitachi). The composition of samples was investigated by energy dispersive X-ray spectroscopy (EDS). The hardness of samples, defined as the resistance offered by the material to indentation, i.e., to permanent deformation and cracking, was analyzed using a Vickers micro hardness test machine.

3. Results and Discussion

Figure 1 shows the θ-2θ XRD patterns of the ZrO_2 films sprayed on Co-Cr-Mo alloys after sintering at 750, 900, and 1100 °C. It was found that γ(111), γ(200), and γ(220) diffraction peaks were located at 2θ positions of 43.91, 51.23, and 75.47°, respectively, for all samples. These three diffraction peaks were indexed to the Co metal phase of the Co-Cr-Mo alloy. As the sintering temperature was increased to 750 °C, two diffraction peaks with very low intensities appeared: tetragonal ZrO_2(101) and monoclinic ZrO_2(021), located at the 2θ positions of 29.79 and 38.64°, respectively. When the ZrO_2-coated Co-Cr-Mo sample was sintered at 900 °C, the diffraction peak of tetragonal ZrO_2(101) disappeared. However, a phase of tetragonal ZrO_2(110) appeared (the peak located at a 2θ position of 34.91°), while the phase of monoclinic ZrO_2(021) was still

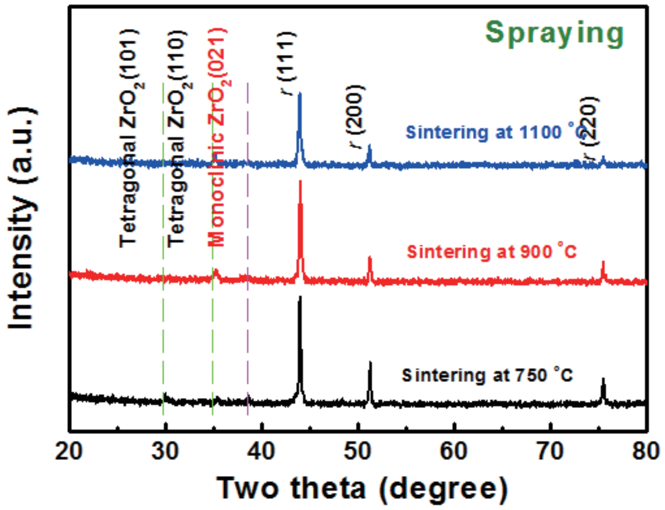


Fig. 1. (Color online) XRD patterns of ZrO_2 sprayed on Co-Cr-Mo substrates after sintering at 750, 900, and 1100 °C.

weak. When the sintering temperature was further increased to 1100 °C, only the tetragonal (110) phase existed in the ZrO_2 film (the monoclinic ZrO_2(021) phase disappeared).

Figure 2 shows the θ-2θ XRD patterns of the screen-printed ZrO_2 layers on Co-Cr-Mo alloys after sintering at 750, 900, and 1100 °C. It can be seen that the diffraction peaks of γ(111), γ(200), and γ(220) also appeared for these samples. When the ZrO_2-coated Co-Cr-Mo sample was sintered at 750 °C, there was no diffraction peak of the ZrO_2 phase. Upon further increasing the sintering temperature to 900 and 1100 °C, both the tetragonal ZrO_2(110) and monoclinic ZrO_2(021) phases appeared in these two samples. Compared with the XRD results shown in Fig. 1, the intensities of the tetragonal ZrO_2(110) and monoclinic ZrO_2(021) diffraction peaks appearing in the Co-Cr-Mo alloys coated with the screen-printed ZrO_2 layers (sintered at 900 and 1100 °C) are clearly higher than those for the samples coated with the sprayed ZrO_2 layers.

Figures 3(a)–3(c) show plan-view SEM images of screen-printed ZrO_2 on Co-Cr-Mo substrates after sintering at 750, 900, and 1100 °C, whereas plan-view SEM images of sprayed ZrO_2 on Co-Cr-Mo substrates after sintering at 750, 900, and 1100 °C are shown in Figs. 3(d)–3(f), respectively. At the sintering temperature of 750 °C, there were no thick-plate structures, and equiaxed rhombohedral columnar structures formed on the sample surface for both deposition methods. There were also a few thin-plate structures on the surfaces of these two samples. When the sintering temperature was increased to 900 and 1100 °C, a large number of thick-plate and equiaxed rhombohedral columnar structures were precipitated and formed on the sample surface for both deposition methods, whereas these microstructures were not observed in the ZrO_2 slurry (not shown here). This indicates that the thick-plate and equiaxed rhombohedral columnar structures were formed during the sintering at 900 and 1100 °C. Moreover, these structures became more prevalent with increasing sintering temperature.

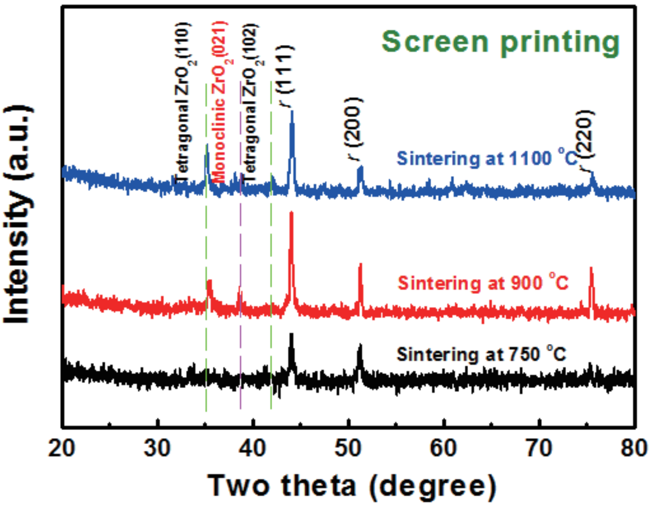


Fig. 2. (Color online) XRD patterns of the screen-printed ZrO_2 on Co-Cr-Mo substrates after sintering at 750, 900, and 1100 °C.

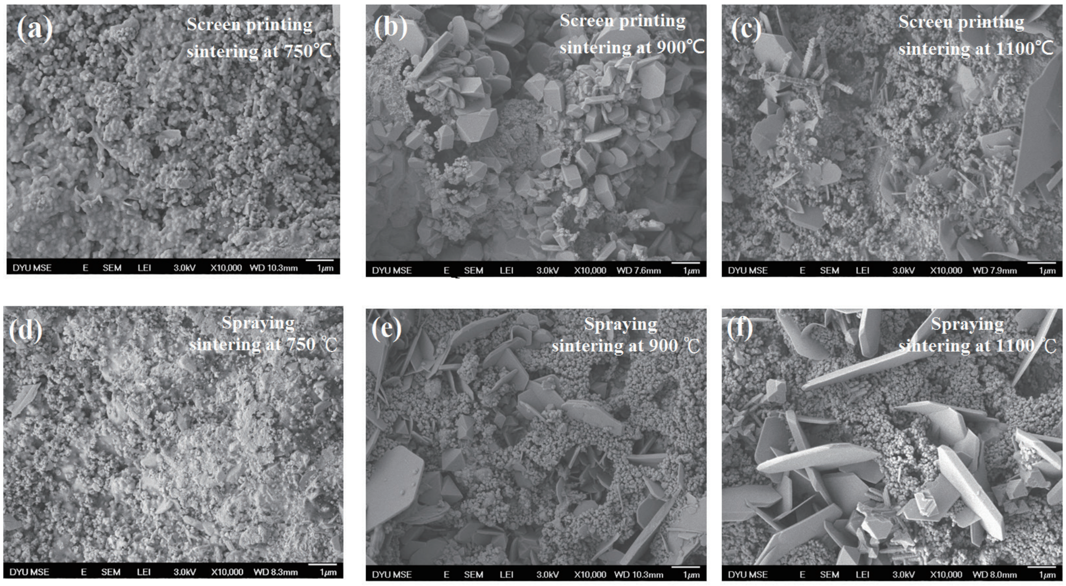


Fig. 3. Plan-view SEM images of screen-printed ZrO_2 on Co-Cr-Mo substrates after sintering at (a) 750, (b) 900, and (c) 1100 °C. Plan-view SEM images of ZrO_2 sprayed on Co-Cr-Mo substrates after sintering at (d) 750, (e) 900, and (f) 1100 °C.

Additionally, Figs. 4(a)–4(c) show cross-sectional SEM images of screen-printed ZrO_2 on Co-Cr-Mo substrates after sintering at 750, 900, and 1100 °C, while cross-sectional SEM images of ZrO_2 sprayed on Co-Cr-Mo substrates after sintering at 750, 900, and 1100 °C are displayed in Figs. 4(d)–4(f), respectively. For the sintering temperatures of 750, 900, and 1100 °C, the ZrO_2 thicknesses of the screen-printed samples were evaluated to be 2.36, 2.56, and 3.78 μm,

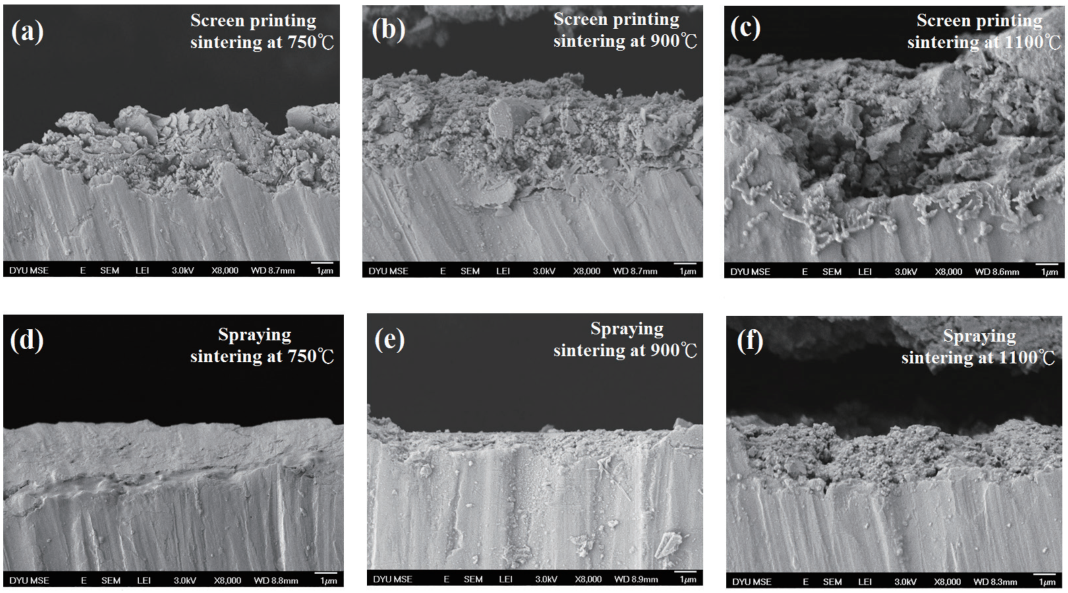
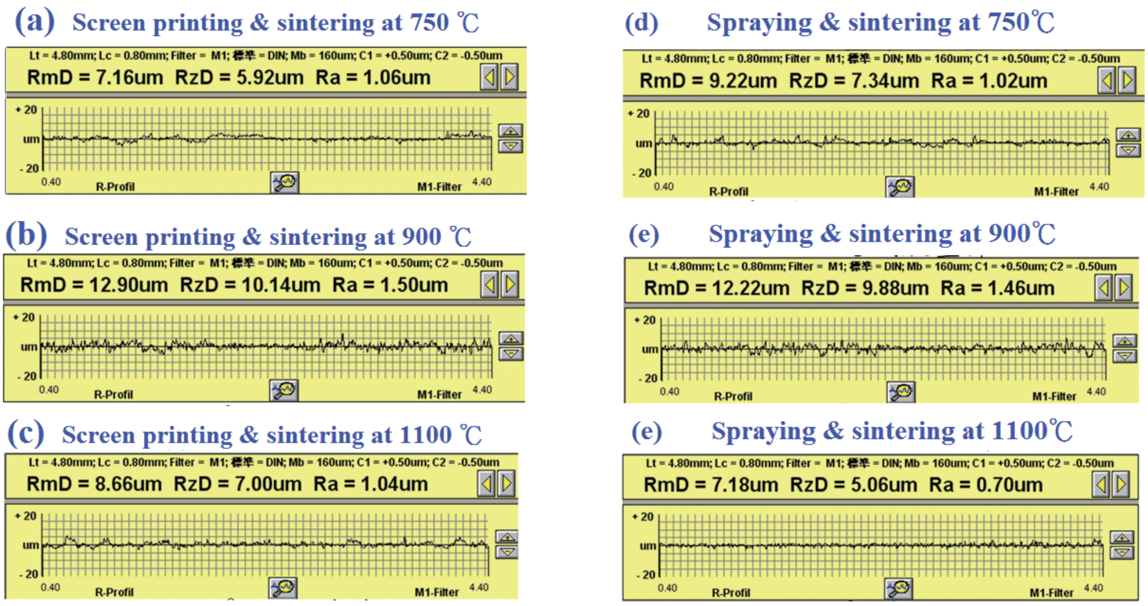


Fig. 4. Cross-sectional SEM images of screen-printed ZrO_2 on Co-Cr-Mo substrates after sintering at (a) 750, (b) 900, and (c) 1100 °C. Cross-sectional SEM images of ZrO_2 sprayed on Co-Cr-Mo substrates after sintering at (d) 750, (e) 900, and (f) 1100 °C.

while the thicknesses of the sprayed samples were 1.52, 2.17, and 2.68 μm, respectively. The screen-printed samples were thicker than the sprayed samples. The ZrO_2 film thickness also increased with the sintering temperature.

Figures 5(a)–5(c) show the R_a values of screen-printed ZrO_2 on Co-Cr-Mo substrates after sintering at 750, 900, and 1100 °C, while the R_a values of ZrO_2 sprayed on Co-Cr-Mo substrates after sintering at 750, 900, and 1100 °C are shown in Figs. 5(d)–5(f), respectively. For the sintering temperatures of 750, 900, and 1100 °C, the R_a values of the ZrO_2 films prepared by screen printing were 1.06, 1.50, and 1.04 μm, respectively. The sprayed ZrO_2 films had R_a values of 1.02, 1.46, and 0.70 μm, after sintering at 750, 900, and 1100 °C, respectively. The average R_a values of the Co-Cr-Mo alloys coated with ZrO_2 films were all lower than that of the original Co-Cr-Mo substrate slab (R_a: 1.92 μm). Moreover, the samples prepared by spraying were smoother than those prepared by screen printing. Regardless of whether ZrO_2 films are coated by screen printing or spraying, a smoother ZrO_2 film can be achieved after sintering at 1100 °C. In particular, the sprayed ZrO_2 film sintered at 1100 °C had the smoothest surface ($\mathrm{R_a}$: 0.70 μm).

The microhardness values of the samples were measured using a small Vickers hardness machine and are summarized in Table 1. With increasing sintering temperature, the microhardness of the ZrO_2 ceramic films increased, with the sample sintered at 1100 °C having the highest value. The enhanced hardness was attributed to the increased density of the ZrO_2 film after the high-temperature sintering process.


(a) Screen printing & sintering at 750 ℃

Lt = 4.80mm; Lc = 0.80mm; Filter = M1; 標準 = DIN; Mb = 160um; C1 = +0.50um; C2 = -0.50um

RmD = 7.16um RzD = 5.92um Ra = 1.06um

(b) Screen printing & sintering at 900 ℃

Lt = 4.80mm; Lc = 0.80mm; Filter = M1; 標準 = DIN; Mb = 160um; C1 = +0.50um; C2 = -0.50um

RmD = 12.90um RzD = 10.14um Ra = 1.50um

(c) Screen printing & sintering at 1100 ℃

Lt = 4.80mm; Lc = 0.80mm; Filter = M1; 標準 = DIN; Mb = 160um; C1 = +0.50um; C2 = -0.50um

RmD = 8.66um RzD = 7.00um Ra = 1.04um

(d) Spraying & sintering at 750℃

Lt = 4.80mm; Lc = 0.80mm; Filter = M1; 標準 = DIN; Mb = 160um; C1 = +0.50um; C2 = -0.50um

RmD = 9.22um RzD = 7.34um Ra = 1.02um

(e) Spraying & sintering at 900℃

Lt = 4.80mm; Lc = 0.80mm; Filter = M1; 標準 = DIN; Mb = 160um; C1 = +0.50um; C2 = -0.50um

RmD = 12.22um RzD = 9.88um Ra = 1.46um

(e) Spraying & sintering at 1100℃

Lt = 4.80mm; Lc = 0.80mm; Filter = M1; 標準 = DIN; Mb = 160um; C1 = +0.50um; C2 = -0.50um

RmD = 7.18um RzD = 5.06um Ra = 0.70um

Fig. 5. (Color online) Surface roughnesses of screen-printed ZrO_2 on Co-Cr-Mo substrates after sintering at (a) 750, (b) 900, and (c) 1100 °C. Surface roughness results of ZrO_2 sprayed on Co-Cr-Mo substrates after sintering at (d) 750, (e) 900, and (f) 1100 °C.

Table 1
Hardness of Co-Cr-Mo coated with ZrO_2 by screen printing and spraying after sintering at 750, 900, and 1100 °C.

Sintering temperature (°C)	Hardness of Co-Cr-Mo coated with ZrO_2 by screen printing ($HV_{0.5}$)	Hardness of Co-Cr-Mo coated with ZrO_2 by spraying ($HV_{0.5}$)	Hardness of original Co-Cr-Mo ($HV_{0.5}$)
750	683 ± 40	594 ± 41	590 ± 84
900	604 ± 59	595 ± 24	590 ± 84
1100	696 ± 134	767 ± 63	590 ± 84

4. Conclusion

In our work, ZrO_2 films were coated on Co-Cr-Mo substrates by screen printing and spraying. Regardless of whether screen printing or spraying was used, there were many thick-plate and equiaxed rhombohedral columnar structures formed on the sample after sintering at 900 and 1100 °C, whereas only a few thin-plate structures were formed during sintering at 750 °C. After sintering, the surface of the sample coated with the ZrO_2 film was smoother than the original Co-Cr-Mo substrate. With increasing sintering temperature, the hardnesses of the ZrO_2 films deposited by screen printing and spraying were both improved (especially for the sample sintered at 1100 °C), resulting from the enhanced density of the ceramic ZrO_2 films. According to our experimental results, the sprayed ZrO_2 film sintered at 1100 °C possessed the smoothest surface and the highest hardness, which will be helpful for expanding the applicability of medical implants of Co-Cr-Mo alloys. In the future, we will study the sensing performance of ZrO_2 sensors fabricated on Co-Cr-Mo alloys.

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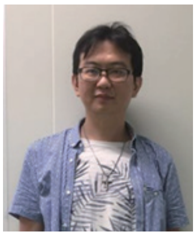

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