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Microstructure and properties of Al_2O_3 and Al_2O_3-ZrO_2 composite coatings on medical NiTi alloy by plasma electrolytic deposition

Miao Wang[1,2]*, Linzhong Zhu[1], Yan Jiang[1], Yongjian Yao[1], Yunlong Wang[1,3]*, Hao Wang[4], Hua Ding[5]
[1]School of Materials Science and Engineering, Jiangsu University, Zhenjiang, 212013, (CHINA)
[2]Institute for Advance Materials, Jiangsu University, Zhenjiang, 212013, (CHINA)
[3]Center for photon Manufacturing Science and Technology, Jiangsu University, Zhenjiang, 212013, (CHINA)
[4]Wall Reform Office, ZhenJiang Housing and Urban-Rural Bureau, Zhenjiang, 212013, (CHINA)
[5]School of Mechanical Engineering, Jiangsu University, Zhenjiang, 212013, (CHINA)
E-mail: Wangmiao@ujs.edu.cn, Wangyunlonghit@aliyun.com

ABSTRACT

Two types of Ceramic coatings were successfully prepared on NiTi alloy by plasma electrolytic deposition in $(NO_3)_3 9H_2O$ and $(NO_3)_3\cdot 9H_2O$+Zr $(NO_3)_4$ electrolytes, respectively. The microstructure and chemical composition of the coatings were characterized. The properties of the coatings including bonding strength, thickness, thermal shock resistance and impact resistance were evaluated. The results showed that the coating obtained in single $(NO_3)_3\cdot 9H_2O$ electrolyte was completely Al_2O_3, and coating obtained in $(NO_3)_3\cdot 9H_2O$+Zr $(NO_3)_4$ electrolyte was composed of Al_2O_3 and ZrO_2. Nearly no Fe element came into the coating. Both coatings showed porous surface and the pores on the surface of Al_2O_3 coating was smaller than those on Al_2O_3-ZrO_2 coating. When increasing the treating time, the coatings almost grew linearly with the maximum thickness of 36μm and 38μm for Al_2O_3 coating and Al_2O_3–ZrO_2 coating, respectively. The bond strength of the coatings gradually increased, whose maximum values of Al_2O_3 coating and Al_2O_3–ZrO_2 coating were 19 and 21 MPa, respectively. For both coatings, with increasing the treating time, the thermal shock resistance first increased and than decreased a little. Al_2O_3 and Al_2O_3-ZrO_2 coatings treated with different time showed similar impact resistance. The impact resistance of the coating increased when the surface porous layer was polished off.

KEYWORDS

Al_2O_3 coating; Al_2O_3-ZrO_2 composite coatings; Plasma electrolytic deposition; NiTi alloy.

INTRODUCTION

Nickel titanium (NiTi) is a near-equiatomic intermetallic that possesses attractive properties such as superelasticity, shape memory effect and biocompatibility[1-4] and it is widely used in biomedical fields. It is usually used as cardiovascular stents and staples of broken bones for its superelasticity properties and shape memory effect. However, NiTi has always been facing the problem of corrosion which result in leakage of nickel ions in vivo and hence cause cytotoxic reactions. Therefore, it is of great importance to improve the corrosion resistance of the NiTi alloy and suppress the leakage of nickel ions. Surface treatments have been proved to be an effective method prevent the leakage of nickel ions[5-6].

Plasma electrolytic deposition (PED) is a plasma-assisted electrochemical technique for surface treatment of metals, especially these so called valve metals such as Ti, Al, Mg, Nb, etc[9-11]. It can be used to fabricate ceramic coatings with high corrosion resistance on metal surface. PED coatings for biomedical application with desirable properties has been obtained on some biomedical metal such as Ti and it alloy and Mg and it alloy[9-10]. The coatings usually showed high bonding strength to the substrate and the micrometer-scale porous surface is suitable for implant fixation[12].However, due to the limitation of the technique itself, most PED studies are concentrated on biomedical Ti and Mg and very few PEO studies have been focus on NiTi alloy[13]. PED is usually suitable for treatment of valve metals such as Ti, Al, Mg and metals possessing much other metal elements such as Fe, Cr, Ni are thought to be difficulty to be subjected to PEO. Formation of oxide layers by PEO on NiTi is relatively difficult compared to Ti, Al, Mg[14-15]. PEO process on non-valve metals usually need pretreatment to first deposit valve metal coating on their surface and then subjected to common PED treatment. Recently, our group development a derivative process called cathodic plasma electrolytic deposition to directly prepare coatings on metals. Experiments proved that many kinds of metals such as stainless steel, iron, Ti, Al, Mg, ect and their alloys could be subjected to CPED and the corrosion resistance of the substrate metal could be improved. This article deal with the CPED process on NiTi alloy and Al_2O_3 and Al_2O_3-ZrO_2 composite coatings were obtained on its surface. The microstructure and corrosion resistance of Al_2O_3 coating was studied.

EXPERIMENTAL PROCEDURE

Coating preparation

Rectangle (15 mm ×15 mm × 0.2 mm) NiTi alloy were used as substrates in CPED. The PEO system contains a single-polar pulsed electrical power source, stainless steel electrolytic bath (also served as anode), PTFE stirrer and cooling system. The super alloys substrate were subjected to PEO in two types of electrolyte: the absolute ethanol solution of Al $(NO_3)_3 \cdot 9H_2O$ (18g/l) and Al $(NO_3)_3 \cdot 9H_2O$ (18 g/l) + Zr $(NO_3)_4$ (4 g/l), respectively. The electric parameters were: current density used 6 A/dm^2, the duty ratio was 40%, the frequency 3000 Hz. In each electrolyte, the PED process lasted 120 min.

Analysis of samples

The morphology and phase composition of the ceramic coatings were investigated by scanning electron microscope (SEM; Hitachi S-570) and X-ray diffractometer (XRD, D/max-rB, Japan, Cu target, Kα radial). The elemental distribution was measured by an energy-dispersive X-ray spectroscopy (EDS, Oxford Model 7537, England). In order to study the properties of the coatings with different treating time, samples treated by 10, 30, 60, 90, 120min were prepared. The bond strength of the coating was determined using a direct pull-off test. During the thermal shock tests, a high temperature kryptol heater was heated up to 300 ℃ and the specimens were put on the kryptol heater keeping for 2 min. Then the specimens were quickly took out and immersed in cool water. The tests were repeated until the ceramic coatings falling off. The falling ball impact tests were employed to evaluate the impact resistance of the coatings, which was carried out with reference to Chinese Stand GB7990-87, 32.5g steel ball to fall to 1.85m height of the center of the coated specimens. When large areas of coating peeling off appears, the number of the impact was use to evaluate impact resistance.

RESULTS AND DISCUSSION

Characterization of the coating

Phase composition of coating The XRD spectra of coatings obtained in two types of electrolytes are displayed in Figure1. It can be noticed that coating obtained in Al $(NO_3)_3$ electrolyte is composed of crystal Al_2O_3. Both α-Al_2O_3 and γ-Al_2O_3 are presented in the coating and α-Al_2O_3 are much more than γ-Al_2O_3. For coating obtained in Al $(NO_3)_3$+Zr $(NO_3)_4$ electrolyte, the XRD spectra reveals that apart from Al_2O_3, ZrO_2 crystal phase is also found in the coating. The ZrO_2 is in the form of c-ZrO_2 and Al_2O_3 also occurs in the form of both α-Al_2O_3 and γ- Al_2O_3 but γ- Al_2O_3 is very little compared to that of coating obtained in Al $(NO_3)_3$. That is to say, coating obtained in Al $(NO_3)_3$ solution is nearly a single species of Al_2O_3, the composition of which is much α-Al_2O_3 plus some γ-Al_2O_3. Adding Zr $(NO_3)_4$ in the electrolyte can not only induce ZrO_2 crystal into the coating, but also deduce the contents of γ- Al_2O_3, which is the relatively unstable phase. This will be help for increasing the performance of the coating in most cases.

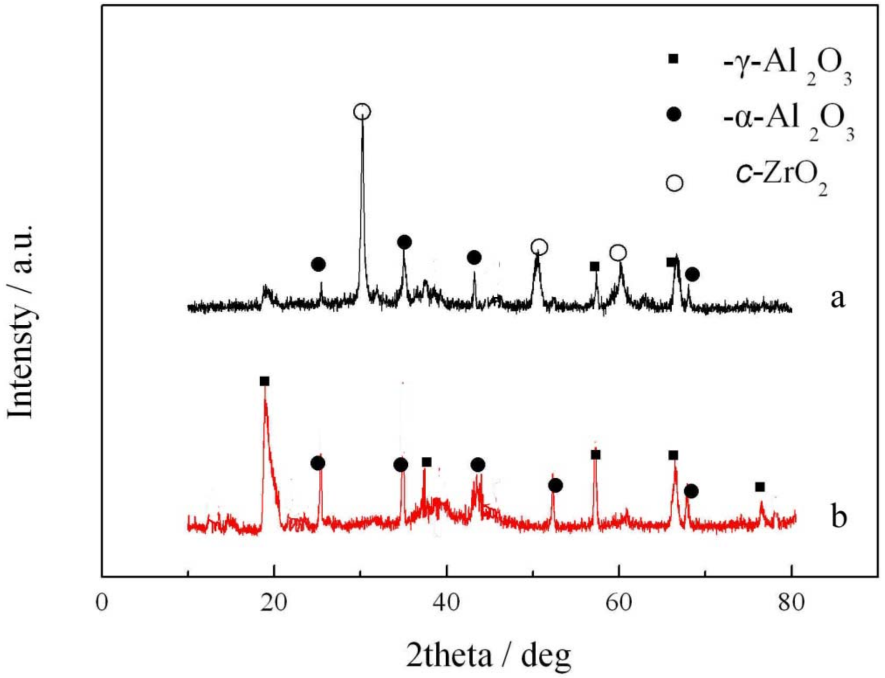

Figure 1 : XRD pattern of PEO coating obtained in (a) Al (NO_3)$_3$ and (b) Al (NO_3)$_3$ +Zr (NO_3)$_4$

The elementals composition of the coating The surface EDS spectra of coatings obtained in two types of electrolytes are shown in Figure 2. It can be seen that the coating obtained in Al (NO_3)$_3$ solution consists of Al, O element and coating Al (NO_3)$_3$ + Zr (NO_3)$_4$ solution consists of Al, O and Zr elements. The main element of super alloy substrate namely Fe is seldom detected by surface EDS analysis. Other elements with relatively higher contents in the substrate such as Ni and Cr are also not found on the coating surface.

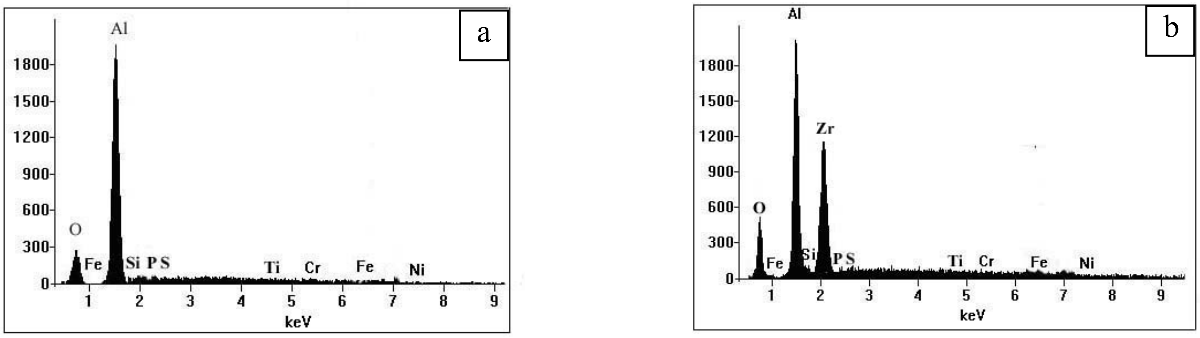

Figure 2 : Surface EDS spectra of coatings obtained in (a) Al (NO_3)$_3$ and (b) Al (NO_3)$_3$ +Zr (NO_3)$_4$

In order to further analysis the Fe elements in the substrate whether come into the coating, the EDS spectra of coating (obtained in Al (NO_3)$_3$) cross section of the some elements of are given Figure 3. It depicts that the Al, O elements appear in the whole cross section of the coating, while the Fe element quickly decreased from the substrate side across the interface to the coating side. Only a little Fe appeared in the interface near the coating side. So it can be conclude that no large amount come into the body of the coating. Here the result is different from many results of PEO coatings on valve metals and their alloys[7,11-12], as the substrate samples here were used as cathode. Few Fe in the interface might transfer from the substrate to coating during the discharge reaction in the plasma environment with high temperature.

Morphology of the coatings The SEM photo of outer surface and inner surface morphology of the two kinds of coatings are shown in Figure 4. The areas marked Ⅰ and Ⅱ in Figure 4 (a) and (b) are outer surface and inner surface, respectively. Figure 4 shows that for both coatings, the out surface is covered by many micro-pores. There are a great deal of fuse mass piles around the pores. PEO, as a plasma enhanced deposition with discharge, it is agreed widely that the pores are rudimental discharge channels in the discharge reaction and the fuse mass around the pores are melts round the channels mouth which were formed quickly by the cooling of the electrolyte[13-14]. It can also be seen that the pores on Al_2O_3-ZrO_2

coating surface are a little small than those on Al_2O_3 coating. So, it can be concluded that adding Zr $(NO_3)_4$ in Al $(NO_3)_3$ solution can decrease the pores on the coating surface.

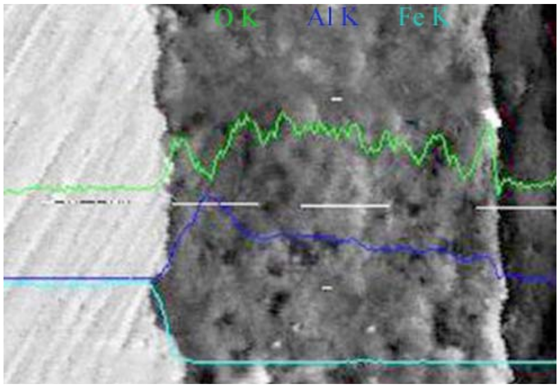

Figure 3 : Cross section EDS spectra of coatings obtained in Al $(NO_3)_3$

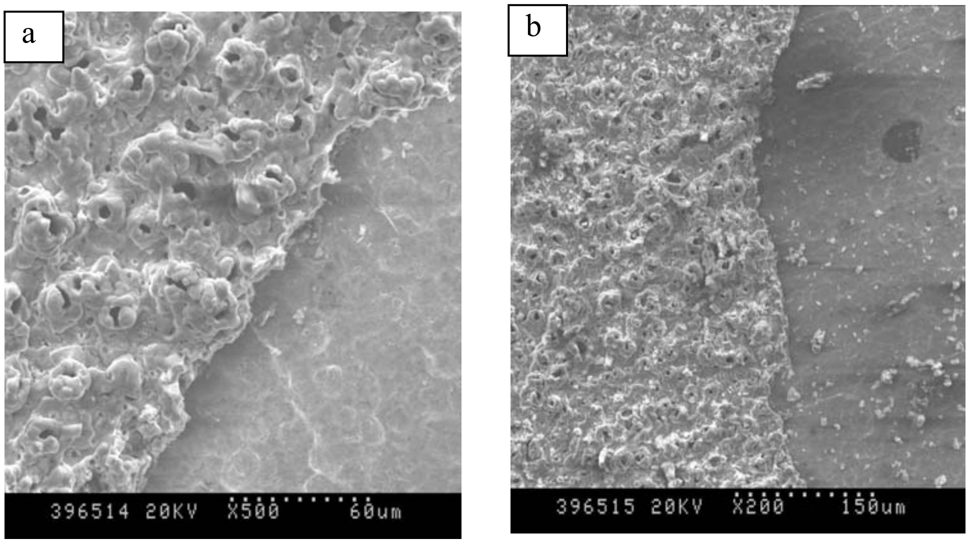

Figure 4 : The SEM photo of outer surface an inner surface morphology of the coatings Obtained in (a) Al $(NO_3)_3$ and (b) Al $(NO_3)_3$ +Zr $(NO_3)_4$

It was reported that coating prepared by PEO technique are usually a surface porous structure, not a body porous structure[15]. So, in order to further study the inner surface of the coating, the outer surface of the coatings were peeled off (about 10 μm) and the inner surface was obtained as was shown in Ⅱ area in Figure 4 (a) and Figure 4 (b). The Ⅱ area tells that there were no pores were found on the inner surface. The above analysis improve that Al_2O_3 and Al_2O_3-ZrO_2 coatings on super alloy were surface porous and course and inner of the coating were dense.

Properties of the coatings

Thickness of coatings The thickness of two types of coating varies with the treating time are list in Figure 5. It can be seen that the coating grows nearly linearly when increasing the treating time with little growth rate at the end of treating process. This growth regularity is similar to PEO coatings. In addition, the Al_2O_3 coating is a little thicker than the Al_2O_3-ZrO_2 coating. The maximum of thickness of the Al_2O_3 coating 38μm, and the value of Al_2O_3-ZrO_2 coating is 36μm.

Bonding strength of coatings Bonding strength between the coating and the substrate is very important. It is the basic but key factor which affects the working effects of the coating. The Bonding strength of two types of coating varies with the treating time are listed in Figure 6. The bonding strength of coating slightly increased with increasing the treating time. The bonding strength of Al_2O_3-ZrO_2 coating is a little high than that of the Al_2O_3 coating. The maximum bonding strength of the two coatings are obtained when treated with 120 min with the value of 21 MPa for Al_2O_3-ZrO_2 coating and 19 MPa for Al_2O_3 coating. The obtained coatings adhere well to the super alloy substrate. During the repeatedly discharge and cool in local area in the plasma environment of PEO, the interface between the coating/substrate is usually irregular and staggered (also can be seen form Figure 3), which is beneficial of increasing the bonding strength of the coating.

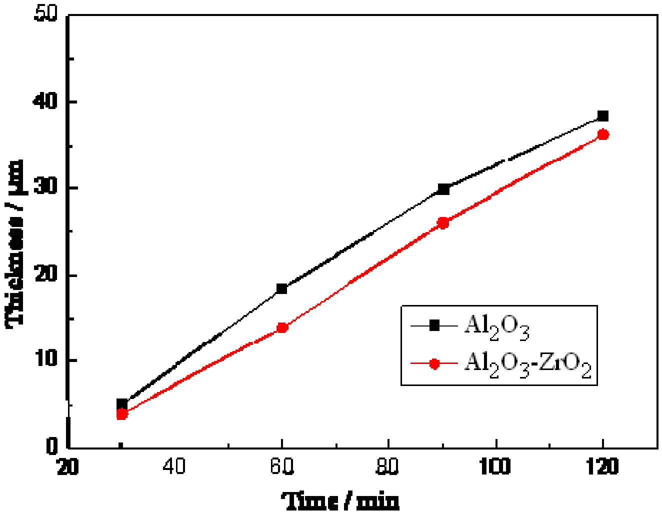

Figure 5 : Thickness of coatings vary with treating time

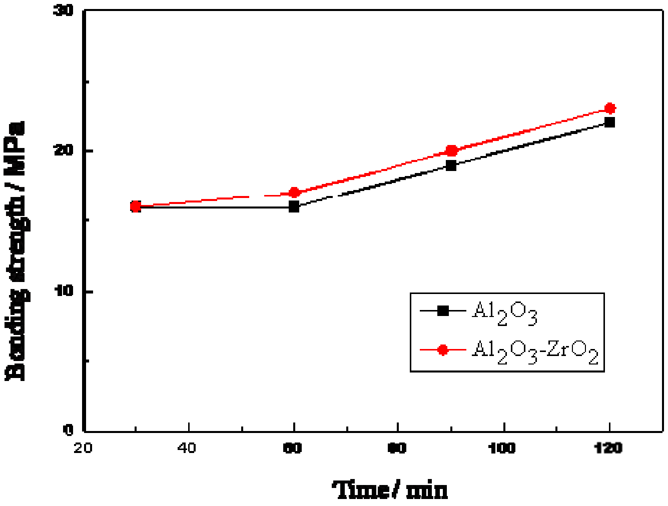

Figure 6 : Bonding strength of coatings vary with treating time

Thermal shock resistance of the coatings Most super alloys are used in aerospace fields. The working conditions usually required them to have a good thermal shock resistance. So the thermal shock resistance tests were employed here. The tests results of the two types coated samples are shown in TABLE 1. The results reveal that Al_2O_3 coating and Al_2O_3-ZrO_2 coating exhibit the same change tendency of thermal shock resistance. With increasing the treating, the thermal shock resistance first increase and than decrease a little. But the Al_2O_3-ZrO_2 coating show a little better thermal shock resistance than the Al_2O_3 coating, especially for samples treated with long time. Better thermal shock resistance of Al_2O_3-ZrO_2 coating might be attributed to composition the coating. There are less unstable phase of γ-Al_2O_3 in the coating which may result in the destruction of the coating during the thermal shock resistance tests.

TABLE 1 : Thermal shock resistance tests results of coatings with different treating time

Treating time (min)	**Number of shock cycles**	
	Al_2O_3 coating	**Al_2O_3–ZrO_2 coating,**
30	5	5
60	8	10
90	11	13
120	9	10

The falling ball impact tests The results of impact resistance tests of coatings treated with different time are listed in TABLE 2. For coatings treated with 120 min of both coatings, another falling ball impact tests was carried. The surface was first stripped 10μm and followed by the common tests. The results are also listed in TABLE 2. It can be seen that with increasing the treating time, the impact resistance of the coatings gradually increases. Al_2O_3 and Al_2O_3-ZrO_2 coatings show similar impact resistance. However, when polished off the porous surface, the number of impact times increased of both coatings. This may because the inner surface is denser than the outer surface. The porous surfaces are easily to be destroyed.

TABLE 2 : Falling ball impact tests results of coatings with different treating time

Treating time (min)	**Impact times**	
	Al_2O_3 coating	Al_2O_3-ZrO_2 coating,
30	3	3
60	5	5
90	6	7
120	8	8
120(polished off 10um)	9	12

CONCLUSION

Al_2O_3 and Al_2O_3–ZrO_2 coatings with porous surface were fabricated on NiTi by cathodic plasma electrolytic deposition. The coatings almost grew linearly with treating time with the maximum thickness of 36μm and 38μm for Al_2O_3 coating and Al_2O_3–ZrO_2 coating, respectively. The bond strength of the coatings gradually increased and maximum values of Al_2O_3 coating and Al_2O_3–ZrO_2 coating were 19 and 21 MPa, respectively. The thermal shock resistance first increased and than decreased a little with increasing the treating time. Al_2O_3 and Al_2O_3-ZrO_2 coatings treated with different time showed similar impact resistance and impact resistance increased when the surface porous layers were polished off.

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