Preparation of ZrO_2/Al_2O_3 composite coating on Ti6Al4V by MAO technology and its oxidation behaviour at 700℃

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Abstract:

High temperature oxidation of titanium has constrained its wider use. It has become a main direction to prepare coating on titanium to improve the anti-oxidation. Coatings prepared by MAO (micro-arc oxidation) technology on Ti6Al4V titanium alloy in three solutions were used to explore the oxidation behaviour. ZrO_2 particle was added in and dispersed by magnetic stirrer at the bottom of electrolyzer in sodium aluminate. Meanwhile potassium fluozirconate within Al_2O_3 particle, sodium metaaluminate mixed potassium fluozirconate were other two solutions. The morphology of surface and interface, phase composition of coatings were studied by SEM, XRD. The oxidation kinetics curve was carried out to describe the oxidation behaviour at 700℃. The result showed that visible different morphology of coatings on surface and interface were characterized. The phase composing were different, however, ZrO_2 and Al_2O_3 are the main phase. By comparison, the coating sample prepared in sodium metaaluminate within ZrO_2 particle showed best oxidation resistance according to thermal cycling oxidation test at 700 ℃ for 100h.

Keywords: Al_2O_3/ZrO_2, MAO, Ti6Al4V, oxidation resistance

Introduction:

Titanium alloys are widely used in aviation and aerospace industries for their low density, high relative strength properties. However the hydrogen and oxygen embrittlement at high temperature restricts their wider application [1]. Therefore surface modifying technology was applied to prepare anti-oxidation coating on titanium to improve the using temperature [2-4]. Micro-arc-oxidation (MAO), often also referred to as plasma electrolytic oxidation (PEO), is an electrochemical formation of anodic films on valve metals (Al, Ti, Mg, Ta, W, Zn and Zr) by spark/arc micro-discharges. Effect of process parameters on coating properties, thermo-mechanical, corrosion resistance and tribological had been studied in references [5-11]. The qualities of MAO coatings were controlled by the composition of the substrate, the nature of the electrolyte, phosphate[12], aluminate[13], silicate[14] are considered to the commonly used electrolyte.

Zirconia toughened alumina (ZTA) material has been widespread concern in recent years for its excellent thermal stability, wear resistance, toughness in tools, dies, biological materials[15-18]. Al_2O_3/ZrO_2 composite coating was studied on valve metals by MAO technolgy in last decades. Al_2O_3/ZrO_2 composite coatings coated on zirconium by MAO

technology were reported while its mechanical, corrosion and wear property were studied [19-21]. On aluminum the Al_2O_3/ZrO_2 composite coatings were mainly prepared in ZrOCl2[22] or K2ZrF6[23] while prepared on magnesium in a mixed solution of NaAlO2, K2ZrF6 and so on[21.24]. Also, the Al_2O_3/ZrO_2 composite coatings were prepared on other metal by kinds of methods [25-28]. Al_2O_3[29.30] and ZrO_2[31.32] coating on Titanium by MAO technology were respectively reported, however the Al_2O_3/ZrO_2 composite coating on it rare reported[33] especially on its oxidation resistance property. In this work, Al_2O_3/ZrO_2 composite coating were prepared on Ti6Al4V alloy by MAO technology with three mixed solutions, and its oxidation resistance property was disscussed.

2. Experiment

2.1 Preparation of coating

The substrate material employed in this investigation was Ti6Al4V titanium alloy with a chemical composition (wt. %) of 6.3 Al, 4.2V, 0.15 O, 0.11 Fe, 0.03 C, 0.02 N, 0.001 H, and Ti balance. The specimens of size 20 mm × 15 mm ×2 mm were ground using 60#, 120#, 400#, 600#, 1000#, 1500# grit silicon carbide papers and cleaned using distilled water and acetone, and then dried in air. For MAO treatment, a pulse power supply was employed, and the Ti6Al4V plate was used as an anode electrode while a graphite plate was used as a cathode in an electrolytic cell. The electrolytic bathes and parameters are show in Tab.1. Micron-Al_2O_3 and ZrO_2 particle was added in electrolyte and dispersed by magnetic stirrer. During the MAO treatment, the temperature of the electrolyte was maintained below 45 ℃. After treatment, the obtained samples were washed with distilled water and dried at room temperature.

Table 1 The electrolyte concentrations and the MAO parameters

Code	Electrolyte components concentration	Voltage /V	Pulse frequency /HZ	Duty ratio /%	Time /min
N-Z	0.1M $NaAlO_2$ +6g/L ZrO_2	450	2000	60	10
K-A	0.02M K_2ZrF_6 +6g/L Al_2O_3	520	2000	60	10
N-K	0.1M $NaAlO_2$ + 0.02M K_2ZrF_6	450	2000	60	10

2.2 Characterization of the coating

The particle size of Al_2O_3 and ZrO_2 were measured by laser diffraction particle size analyzer (LMS-30). The thicknesses of the coatings were measured by eddy current coating thickness gauge at three different points with three measures (TT260, Time Group, Bei Jing). The micro-hardness on surface was measured by micro hardness tester (HXD-1000TMC/LCD) at a load of 10 gF (HV^5_{20}). The phase component of the samples were analyzed with X-ray diffraction (Cu Kα radiation, DMAX-RB, scanning in the range of 2θ=10-80°, 0.02°/step, 40kV, 150mA). Scanning electron microscopy (SEM, FEI Quanta250 Environmental Scanning Electron Microscope) was employed to observe the morphologies.

2.3 Property of the coating

The thermal high-temperature cyclic oxidation test was performed in a kryptol heater furnace at 700℃ in air for 100 h. Ceramic crucible was used to hold sample, and had been pre-heated to a constant weight. The Ti6Al4V substrate and the coated sample, which have already been weighed, were oxidized at 700℃ for 10 h, and then all the specimens were taken out and cooled naturally in air to the room temperature, then weighed again. After that, the samples were put back to the furnace again for another cycle. The test provided 10 times thermal cycles. The kinetic curve of weight variant per unit area versus to time has been got.

3. Result and discussion

3.1 Weight, thickness, hardness and roughness of coatings

The weight, thickness, hardness and roughness of coatings of coatings are showed in Fig.1. The weight gain of sample was recorded by weight before and after MAO process. The weight gain of sample prepared in K_2ZrF_6 with Al_2O_3 (K-A) particle added in expresses largest while N-Z least(Fig.1(a)). The thickness of K-A is about 60 μm while N-Z and N-K are 45 and 35 μm respectively. The hardness of N-K is about 1000HV which is nearly twice over other two samples, while K-A is lowest. The roughness of N-Z is about 6.5 μm, while K-A and K-A are nearly 3.2μm and 2.8μm.

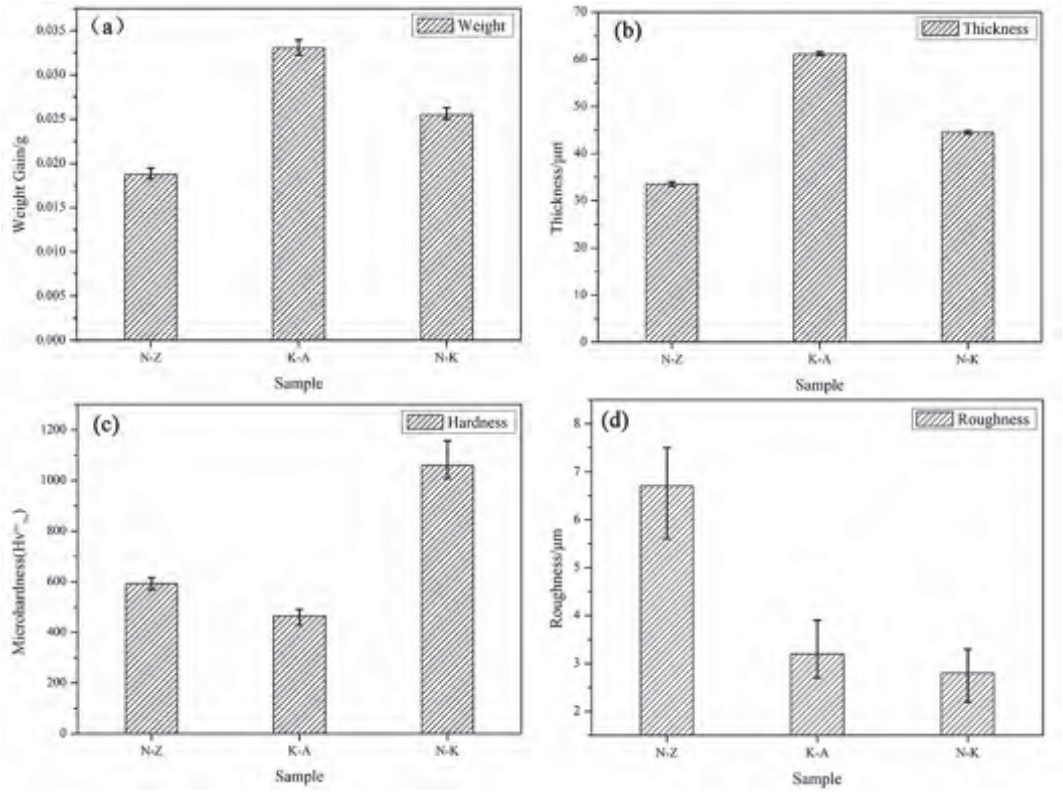
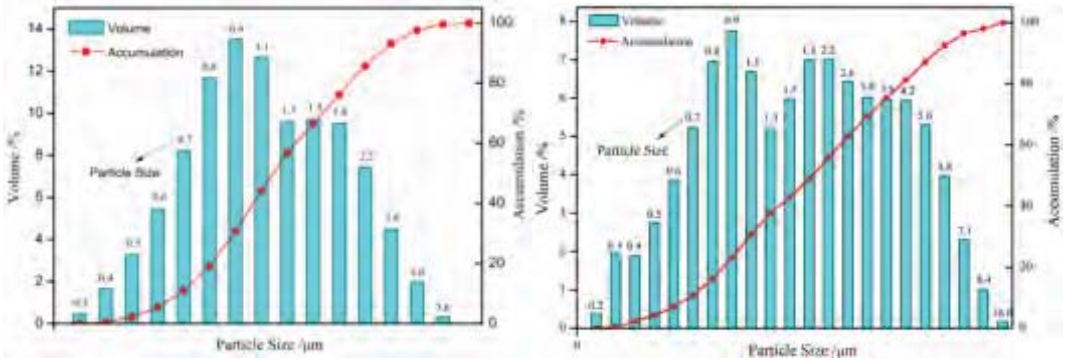


Fig.1 The weight, thickness and hardness of coatings. (a):weight, (b):thickness, (c):hardness

3.2 particle size distribution of Al_2O_3 and ZrO_2 particle

The particle size distribution of Al_2O_3 and ZrO_2 particle is showed in Fig.2. The particle size of Al_2O_3 particle is about 1μm and the distribution is between 0.3μm and 3.6μm(Fig.2(a)) while the distribution of ZrO_2 is from 0.2 μm to 10.0μm(Fig.2(b)). The particle was dispersed by magnetic stirring apparatus on bottom.



(a) (b)

Fig.2 The particle size distribution of Al_2O_3 and ZrO_2 particle, (a):Al_2O_3 particle, (b):ZrO_2 particle

3.3 Micro-morphology of coating

The surface morphology of coatings is showed in Fig.3. Micron-salient features are expressed on the surface of coating prepared in aluminate solution with ZrO_2 particle added in(Fig.3(a)), which are different to the typical micron-pores features. With the addition of

particle in solution, the current decreased and less pores formed on the surface[34]. Relatively flat and smaller micron-pores are the features of MAO coating prepared in the solution of zirconate within Al_2O_3 particle(Fig.3(b)). Evenly distributed micron-pores are found on the surface of coating prepared in mixed aluminate and zirconate solution(Fig.3(c)).

The energy dispersive spectrum (EDS) analysis of local area of coatings are showed in Fig.4. The composition of the salient feature is mostly a combination of aluminum and oxygen. While the composition of gully feature is similar to the salient with the combination of aluminum and oxygen and relatively little titanium(Fig.4(a)). During the MAO process the partial temperature caused by the micro-arc can reach nearly 4000K[35], the meta-aluminate(AlO2-) and hydrion(H+) surround the specimen form the Al_2O_3 and attached on the coating surface. Unlike the description in the report[36], the moving ZrO_2 particle was not found in the coating. The melting ceramic can't catch the moving ZrO_2 particle according to the voltage and decrease of current. The composition of MAO coating prepared in the solution of zirconate within Al_2O_3 particle is the combination of titanium, aluminum, oxygen and zirconium(Fig.4(b)). It can be concluded that the moving Al_2O_3 particle was absorbed into the coating. The composition of MAO coating prepared in a mixed solution of aluminate and zirconate is a combination of titanium, aluminum and oxygen while it is bare of zirconium(Fig.4(c)). Combining the analysis of N-K, zirconium was not found in the coating caused by the lower voltage.

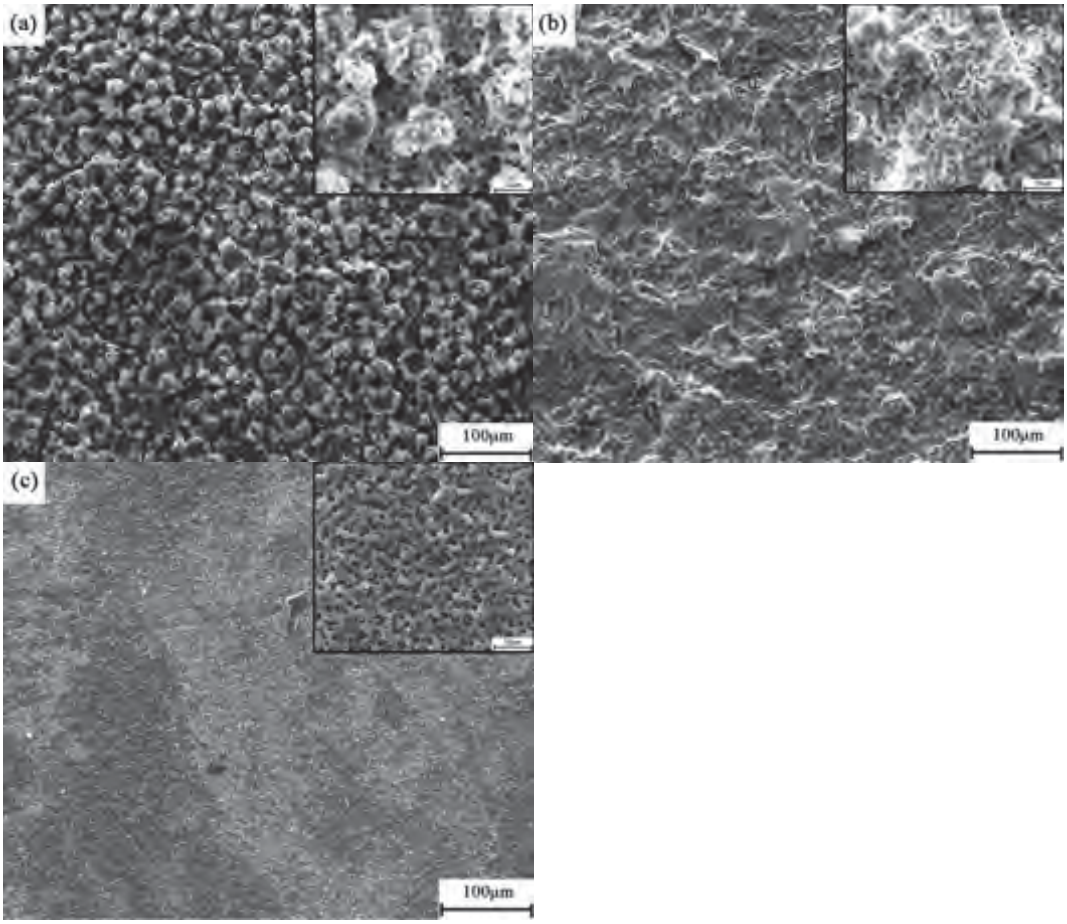


Fig.3 SEM surface morphology of coatings, (a): N-Z, (b): K-A, (c): N-K

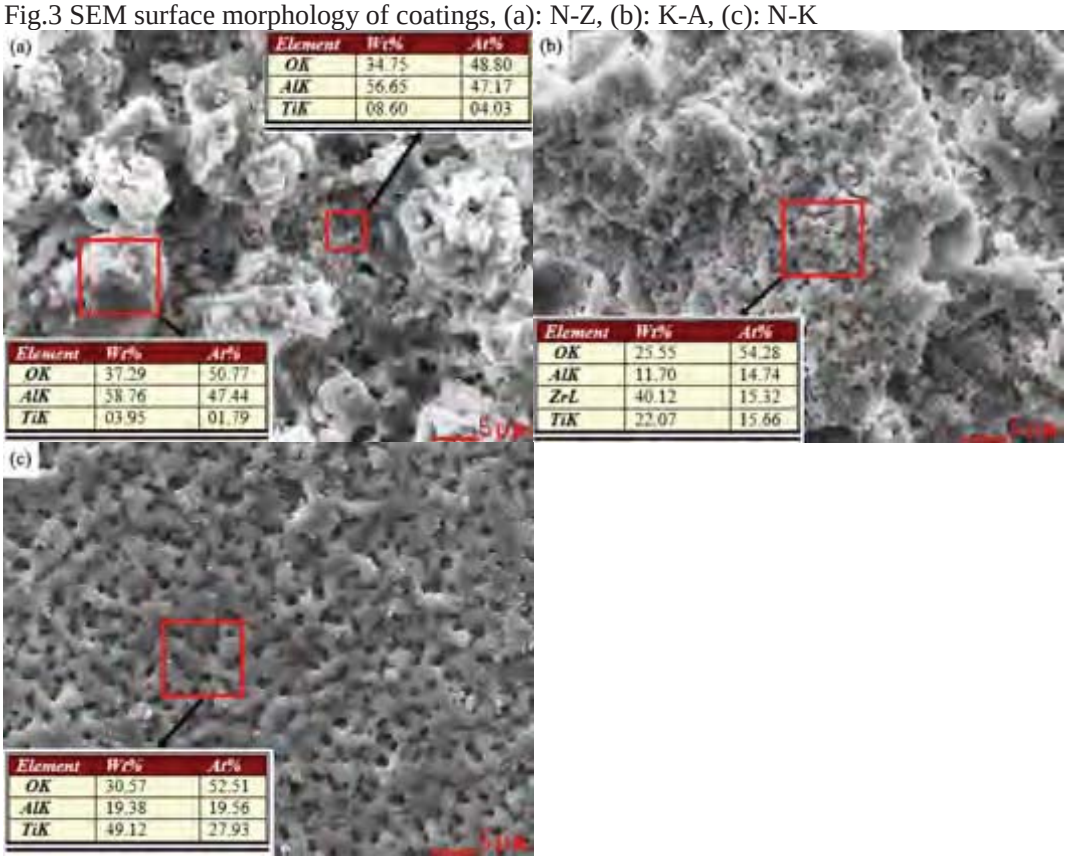


Fig.4 Energy dispersive spectrum (EDS) analysis of local area of coatings, (a): N-Z, (b): K-A, (c): N-K

The section morphology of coatings are showed in Fig.5. Thin inner layer and pours outer layer are the section structure of N-Z(Fig.5(a)). The section structure of K-A is divided into three parts, ragged inner layer-dense layer-porous layer(Fig.5(b)). Single thin layer is found in the coating of N-K(Fig.5(c)).

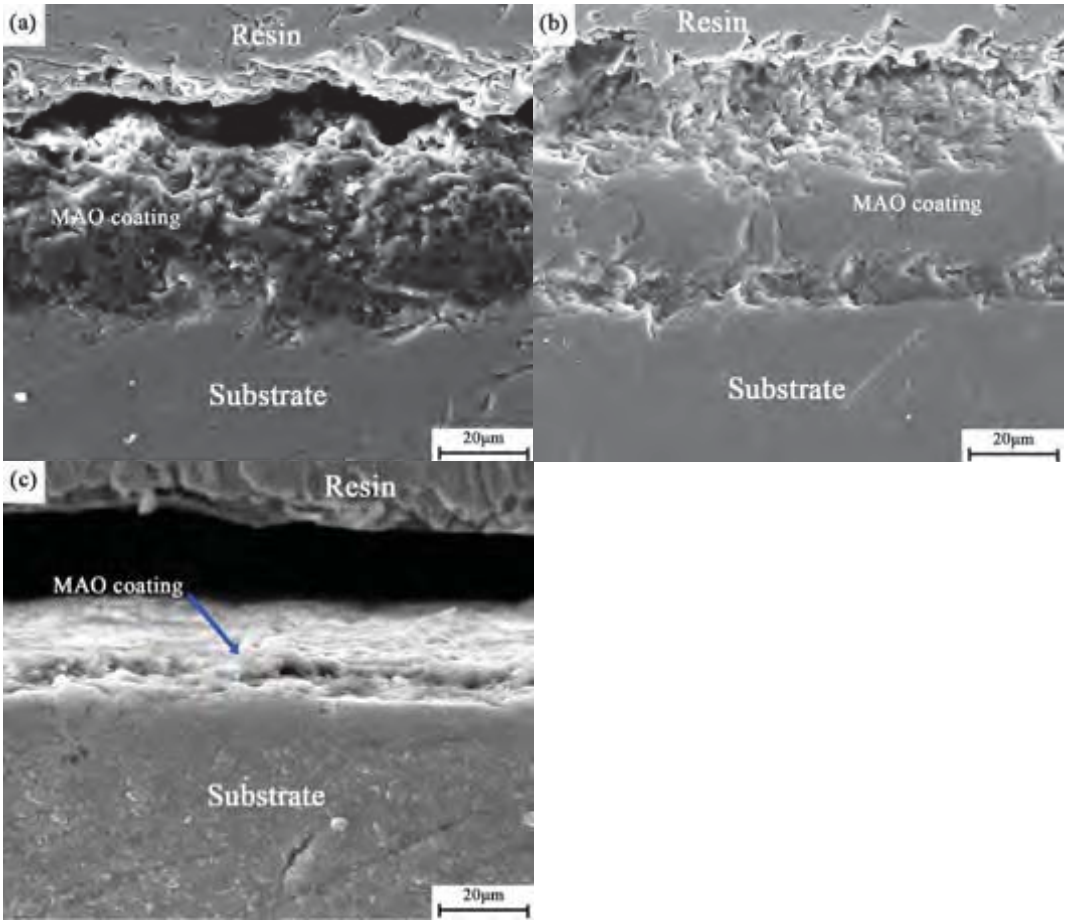


Fig.5 SEM section morphology of coatings, (a): N-Z, (b): K-A, (c): N-K

3.4 Phases of coating

Fig.6 shows the XRD patterns of MAO coatings prepared in different solutions. The composition of N-Z is Al_2O_3 and Ti. Al_2O_3 was formed from the reaction of meta-aluminate(AlO_2^-) and hydrion(H^+) while Ti was sputtered form the substrate into the coating. The MAO coating (N-K) is composed of Al_2O_3, Ti and little ZrO_2 and Ti3O5. ZrO_2 was the decomposition products of zirconate ($ZrF6^{2-}$), while Ti3O5 was the anodizing products. The composition of K-A is mainly ZrO_2 and Al_2O_3. Combining the EDS analysis result (Fig.4(b)), the Al_2O_3/ZrO_2 composite coating was prepared in the solution of zirconate within Al_2O_3 particle.

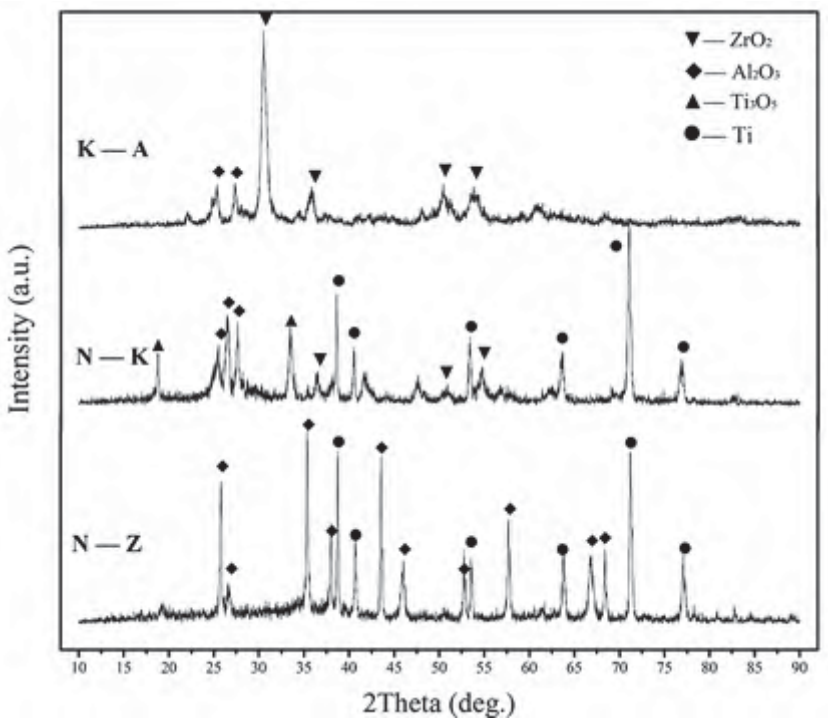


Fig.6 XRD patterns of coatings

3.5 High-temperature oxidation behavor of coating

Fig.7 shows the curves of oxidation weight gain for coating samples and substrate versus time under isothermal cyclic oxidation at 700℃ for 100h. The Ti6Al4V substrate and the samples of N-K and K-A shows similar linear increasing. The MAO coated sample N-K and K-A spalling off with the time contributes to their poor oxidation resistance. However the MAO coating of N-Z shows parabolic increasing with the time, the weight gain is one fifthe compared to Ti6Al4V, which indicates that the MAO coating prepared in aluminate can provide good anti-oxidation resistance for a long time. The ragged inner layer of K-A leads to the spalling off the coating, the thin layer of N-K is not enough to provide anti-oxidation production. Also, the MAO coating prepared in the solution within zirconate is not useful for oxidation resistance. The voltage may plays an important role in the composition of coatings. The moving ZrO_2 particle was not absorbed into the coating as the little micro-arc (N-K). The applied voltage can’t enough make the zirconate to decompose.

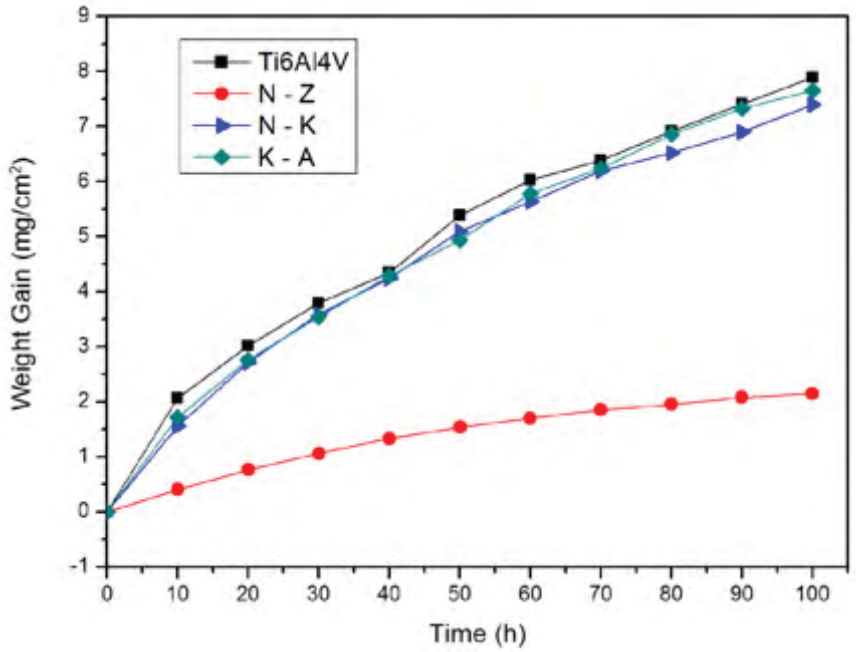


Fig.6 The oxidation kinetics curves of the samples at 700℃ for 100 h

4. Conclusion

Micro-morphology varies with different solution of aluminate within ZrO_2 particle, zirconate within Al_2O_3 particle, mixed aluminate and zirconate. ZrO_2/Al_2O_3 composite coating was prepared in the solution of zirconate within Al_2O_3 particle. The MAO coating prepared in the solution of aluminate within ZrO_2 particle shows good anti-oxidation property at 700℃ for a long time.

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