Effect of (Ta &Nb) on Corrosion Behavior of Nitinol Alloys

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ABSTRACT

In this research, a study of the effect of Ta and Nb additions on the corrosion behavior and properties of Ni-Ti shape memory alloys prepared by powder metallurgy is presented. It was found that; the transformation temperatures and phase structures of the samples prepared consist of martensitic and austenitic phases at room temperature. Also, Vickers hardness values increased with increasing of Ta and Nb additions. Porosity percentages decreased with increasing of addition of Ta and Nb. Finally, the corrosion rate decreased with increasing of Ta and Nb additions.

Keywords: Powder metallurgy, Biocompatibility, Shape memory effect, Ni-Ti alloy, Corrosion rate.

INTRODUCTION

Ti and its alloys have become one of the most attractive biomaterials due to their better corrosion resistance, biocompatibility, good fracture toughness, and relatively low modulus [1-4]. NiTi alloy has become important biomedical materials used in orthopaedic, cardiovascular, urological surgery, and orthodontics [5-9] due to its mechanical (shape memory and superelasticity) and corrosion resistance properties and good biocompatibility [10-12]. Nevertheless, a major concern on the dissolution properties of NiTi alloy still remains owing to the high nickel content; nickel science has been shown to determine several adverse biological effects [13-14]. Usually, NiTi alloys present a superficial thin layer with TiO_2 as the main component [15] protecting them from dissolution, as for commercial pure titanium [16]. The potential of this passive film breakdown is, sometimes very low for NiTi alloys, leading to active dissolution processes. Third alloying element was added to NiTi alloy to enhance its mechanical or corrosion properties.

NiTiNb or NiTiTa alloys have been developed recently as potential orthodontic arch wire materials; unfortunately little published works can be found so far as concerning the corrosion resistance of these alloys in physiological solution [17].

Because of the importance of the NiTi shape memory alloys and their use in important regions within the human body the aim of this study is to prepare NiTi alloys as master alloy and NiTi alloys with different additives of Ta and Nb individually, and study the corrosion behavior of these alloys in different solutions to find out the corrosion behavior of these samples and to determine the period of validity in human body.

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Experimental

The samples were prepared by powder metallurgy from Ni and Ti powders. Powders were produced by Aldrich Chemical Company. The purity and particle size of these powders are shown in Table 1. Ni-Ti powder (master mixture M1; 50 at% Ni with 50 at% Ti and master mixture M2; 51 at % Ni with 49 at % Ti) was mixed by ball mill for two hours. This mixture was used to prepare five groups of samples as shown in Table 2. The samples with Ta and Nb additives were additionally mixed for two hours. After mixing, two master samples of 5 g weight, as discs of 15 mm diameter and about 5 mm height were compacted at 850 MPa by tool steel die. The same procedure was repeated with other sample groups which were compacted at 850 MPa, since this pressure has given the best result in previous studies. All samples were sintered at 950 ºC for 9 h under controlled atmosphere of argon.

X-ray diffraction test was done to identify the formed phases of sintered samples by using XRD instrument type D8 II machine, Bruker axs, 240V, 50Hz and 6.5 KVA made in Germany. Vickers hardness was used to measure the hardness of the sintered samples at loading of 1.0 Kg held for 10 seconds. This test is achieved by using Vickers hardness testing machine type (Fv800 FUTURE-TECH Tester made in Japan).

Porosity measured by using Archimedes method (depending on weighing of sintered samples)

(%) ——— ……. (1)

Where W_s is weight of sample after immersing it in the distilled water for 24 hours, W_d = weight of the dry sample after sintering, and W_n weight of immersed sample in the distilled water and suspended in air.

The transformation temperatures were obtained for the samples using the DSC (Differential Scanning Calorimeter) at a scan rate of 15 ºC/min. The apparatus used to perform this test was DSC type METTLER TOLEDO-Swiss made.

The corrosion test was carried out by potentiostatic technique which contains drawing the cathodic and anodic polarization curves between the potential and current axes; in this test we use two different body solutions; artificial saliva and Ringer's solution (the electrolyte) as shown in the Table 3.Where the temperature of the water bath was fixed at 37 ºC in which the corrosion cell was placed. The test was started when the temperature of the electrolyte reached 37 ºC. The cathodic and anodic polarization curves and corrosion rate was determined at a scan rate of 5 mV/s and a potential range of (-0.25 to 0.25 V), for a sample surface area of 0.78 cm^2. The intersection point of the cathodic and anodic polarization curves tangents gives the corrosion current density (Icorr) which is easily transferred to corrosion rate using faraday's law of electrolysis.

Rmpy = 0.13* Icorr. * Equivalent weight of alloy/ alloy density

Table (1): Purity and particle size of used metallic powders.

Metal (Powder)	Purity (%)	Particle Size (µm)
Ni	99.7	1-10
Ti	99.5	100-200

Ta	99.98	10-50
Nb	99.8	10-50

Table (2): Descriptions of prepared samples

Samples No.	composition	Compaction pressure (Mpa)	Sintering temperature °C	Holding time (H)
1-2	M1 and M2	850	950	9
3-5	M1with 0.1%,0.2% and 0.3 at% of Ta	850	950	9
6-8	M1with 0.1%,0.2% and 0.3 at% of Nb	850	950	9
9-11	M2with 0.1%,0.2% and 0.3 at% of Ta	850	950	9
12-14	M2with 0.1%,0.2% and 0.3 at% of Nb	850	950	9

Table (3): Chemical composition of different body solutions

Solution type	Chemical composition
Artificial saliva	NaCl (0.4g/L), KCl (o.4g/L), $CaCl_2$ (0.78g/L), NaH_2PO_4. H_2O (0.69g/L), Na_2S. $9H_2O$ (0.005g\L), KSCN (0.3g\L), Urea (1g\L).
Simulated body fluid (Ringer's solution)	Adding Ringer tablet to o.5 liter of distillated water and heating the solution to temperature 120°C for 15 min. and leaving it to cool .then Na_2HCo_3 was added to obtain pH of 7.4.Ringer tablet was obtained from Merck Company Germany.

Results and Discussion

The phases produced as a result of the sintering process were investigated using XRD technique. It is seen from figures (1&2), that there are probably no pure metals present which proves that the sintering time and temperature used in this work result in complete sintering reaction. X-ray diffraction showed that all samples alloys consist of martensitic phase (monoclinic) and the austenitic phase (cubic), in addition to Ti_2Ni, and Ni_2Ti. The formation of Ti_2Ni and Ni_2Ti might be attributed to the slow cooling of the samples with the furnace cooling rate whereas, in the sintering condition used throughout this work, the free Gibbs energies for Ni_2Ti and Ti_2Ni were less than that for NiTi and it seems difficult to obtain a final equilibrium structure of NiTi alone, just by solid -state diffusion [18].

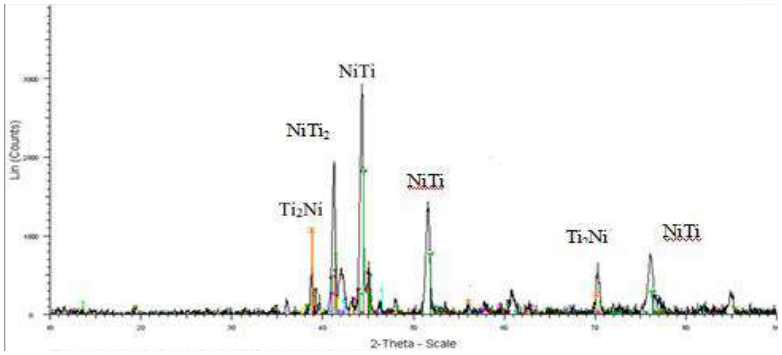

Figure (1): XRD pattern of sample (M1).

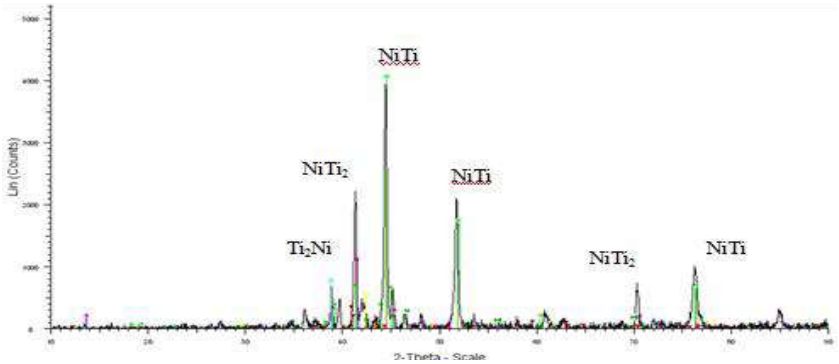

Figure (2): XRD pattern of sample (M2).

The transformation temperatures observation can be seen that all the samples have Mf and Af between -10.4 °C and 47.2 °C as shown in figure (3) which indicates that the samples are a mixture of two phases at room temperature (martensite and austenite) and this is another evidence together with XRD test which proves that the samples of this work consist of martensitic and austenitic phases at room temperature.

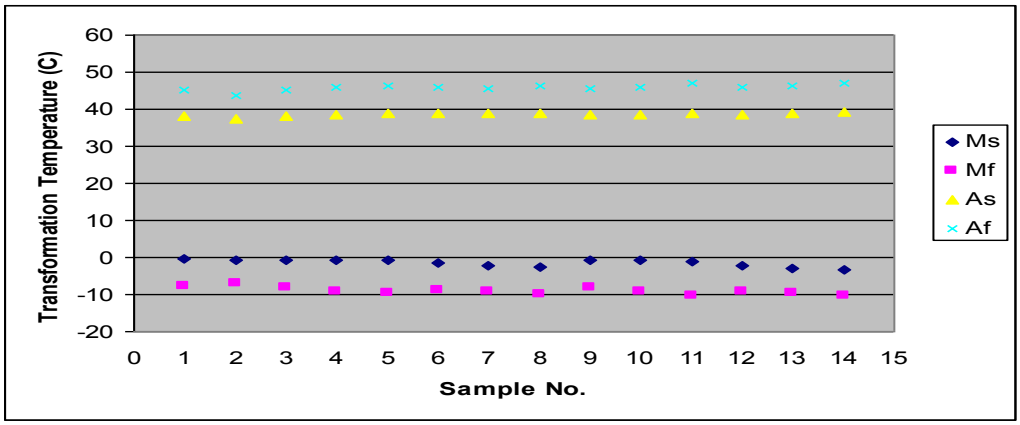

Figure (3): Transformation temperatures of austenitic and martensitic phases of all samples

Figure (4&5) shows that the porosity percentage decreases with increasing the percentages of Ta and Nb additives (0.1, 0.2and 0.3 at%) respectively in booth master

samples (M1&M2) which could be attributed to the better interdiffusion caused by the addition. it is also obvious that the porosity percent of the samples when compacted at 850 MPa which is in good agreement with the expectation; since the compacting pressure leads to good adhesion and interdiffusion between the particles is better which results in more elimination of pores.

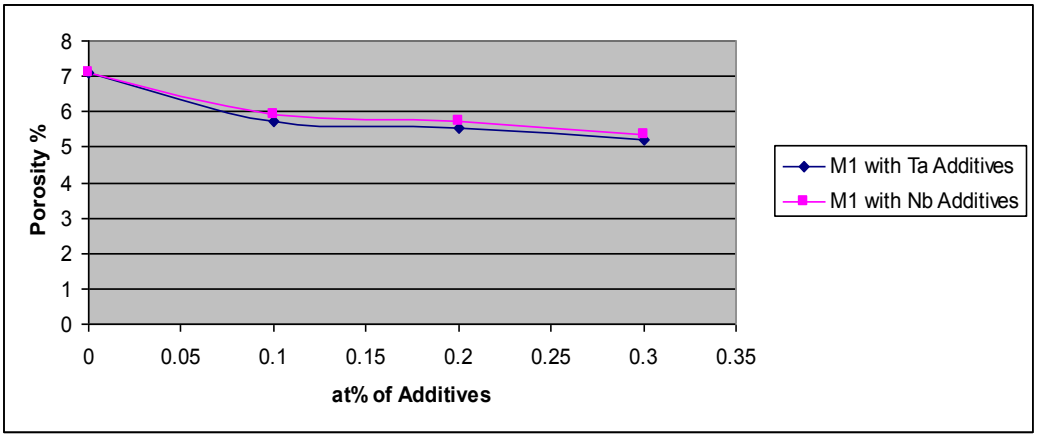

Figure (4): porosity percentage of the master sample (M1) with and without various additives of Ta and Nb.

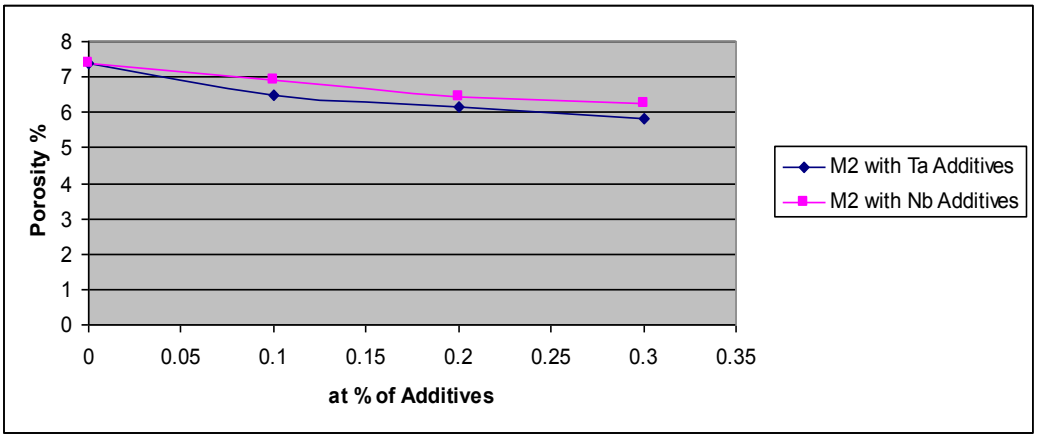

Figure (5): porosity percentage of the master sample (M2) with and without various additives of Ta and Nb.

Hardness measurements were made on master samples (M1&M2) and these values will be compared with those of the prepared samples with additives (Ta and Nb). Figure (6 &7) shows that measurement hardness value of master sample is lower than that of samples with additives. This agrees with the fact that as the compacting pressure leads to the bonding between the particles is better (i.e. better interdifusion) which in turn leads to more pores elimination.

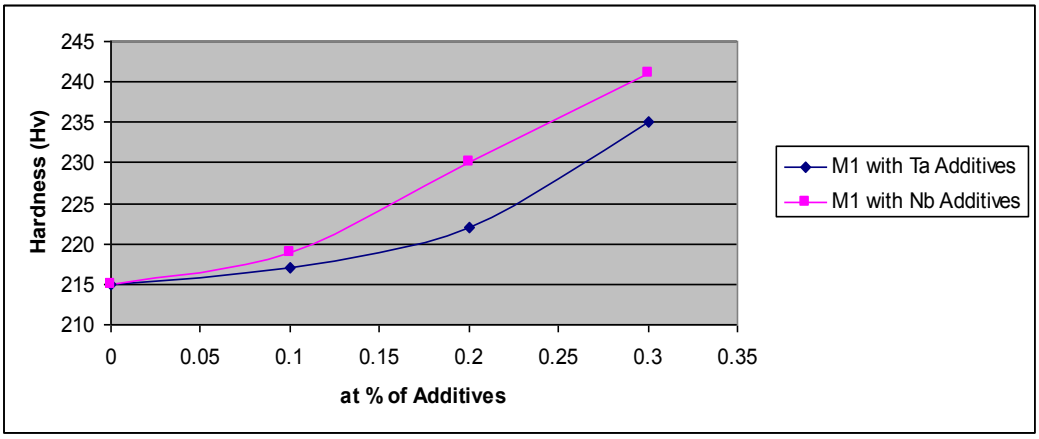

Figure (6): Hardness values of the master sample (M1) with and without various additives of Ta and Nb.

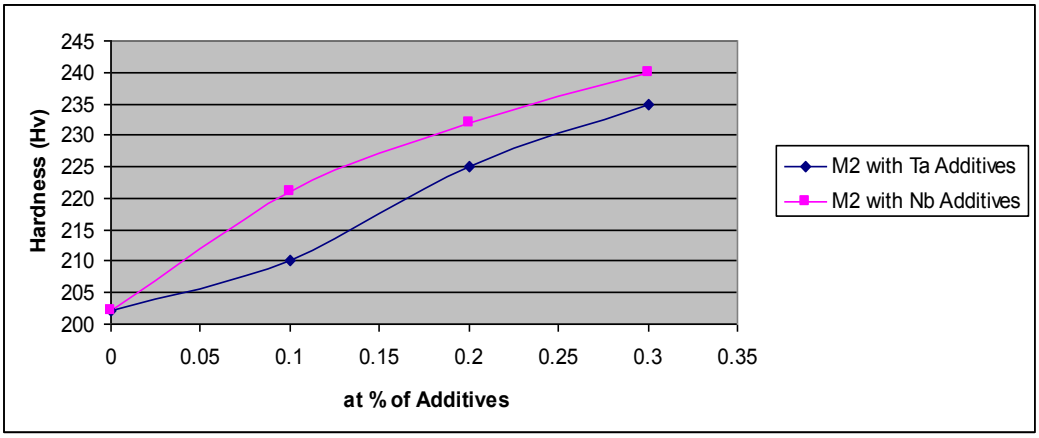

Figure (7): Hardness values of the master sample (M2) with and without various additives of Ta and Nb.

The corrosion behavior was studied using the potentiostat model X MTD-2MA. Both of master alloys M1and M2, have nearly the same corrosion rate, but it is a little bit higher for the M1, which may be due to the higher Ni content in M2 compared to the M1, since Ni is more noble than Ti (from the electrochemical viewpoint) [19-20]. Figs. 1 and 2 indicate that the corrosion rate decreased with increasing the wt% of Ta, this can be attributed to the Ta exhibits higher open circuit potential, wider passive region and higher breakdown potential,[21-22] and so it has an oxide film that improves protection against corrosive media. Figs. 3 and 4 indicate that the corrosion rate decreased with increasing the percentage of Nb. the addition of Nb to NiTi alloy facilitates passivation, produces the more stable passive layer by reducing anodic current density, and finally promotes the corrosion resistance [23].

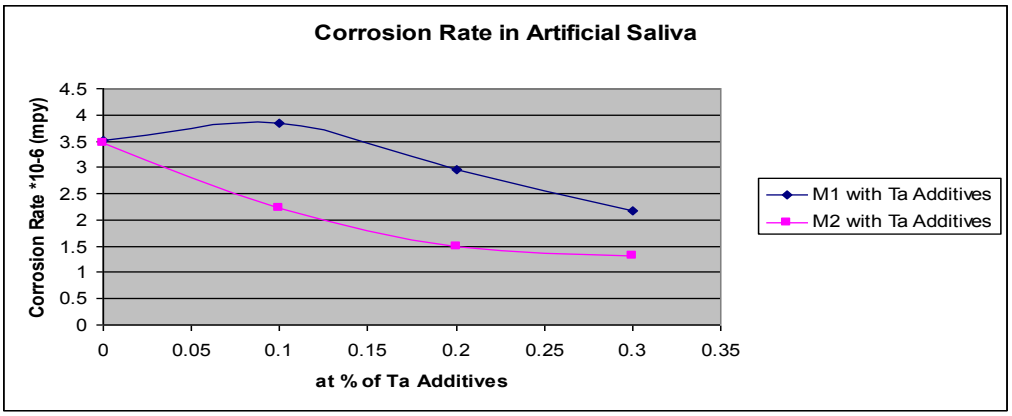

Figure (8): Corrosion Rate (mm/yr) for the samples with and without Ta additives in saliva solution

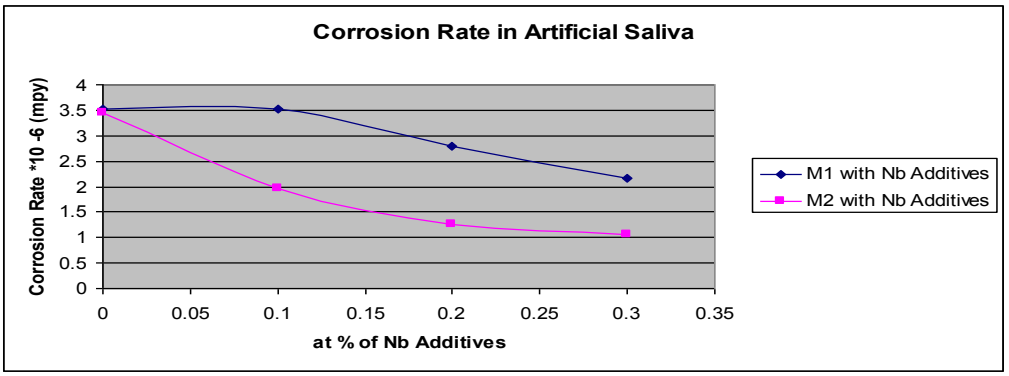

Figure (9): Corrosion Rate (mm/yr) for the samples with and without Nb additives in saliva solution

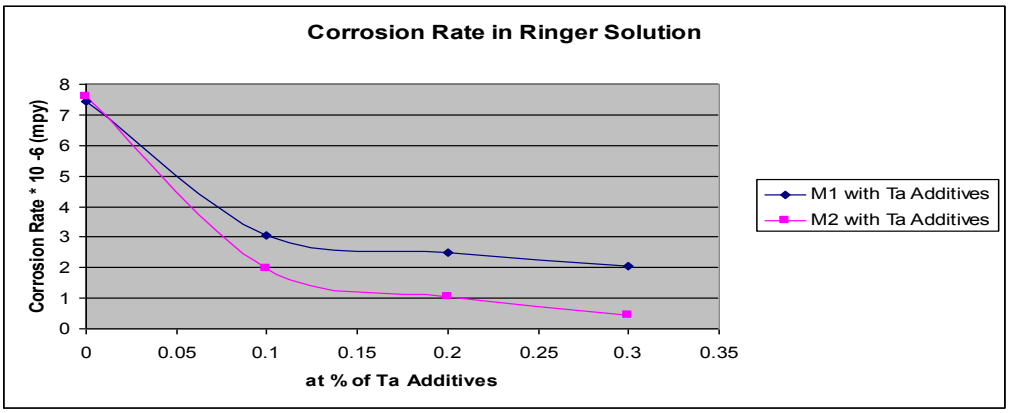

Figure (10): Corrosion Rate (mm/yr) for the samples with and without Ta additives in ringer solution

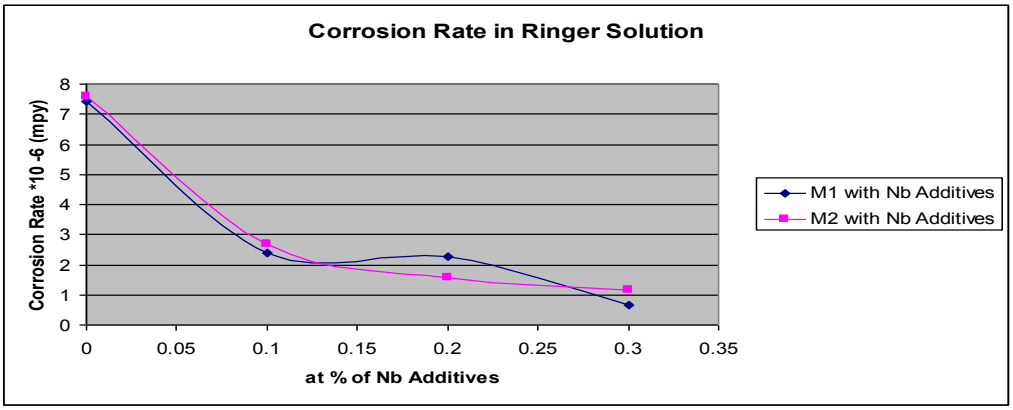

Figure (11): Corrosion Rate (mm/yr) for the samples with and without Nb additives in ringer solution

CONCLUSION

1-The samples sintered at 950 °C for 9 hours result in a two-phase structure (austenite and martensite) at room temperature. The samples with Ta and Nb additions also resulted in the same two-phase structure at room temperature.

2-Increasing Ta and Nb addition results in a considerable decrease in the porosity and increase in the hardness compared to the master samples.

3-Tissues in the human body contain water, dissolved oxygen, proteins and various ions, such as chloride and hydroxide, and they present an aggressive environment to metals or alloys used for implantation. So in this research NiTi corrosion behavior can be significantly improved by the addition of Nb and Ta with different percentage.

4-Ta exhibits higher open circuit potential, wider passive region and higher breakdown potential.

5-Nb produces the more stable passive layer by reducing anodic current density, and finally promotes the corrosion resistance.

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