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Zirconium Oxide Deposition on Titanium

G.Sheela and Malathy Pushpavanam
Central Electrochemical Research Institute, Karaikudi-630 006,India

Zirconium oxide gel was deposited on titanium from zirconyl nitrate and zirconyl chloride baths. These coating are then annealed to produce zirconium oxide coatings. The effect of metal concentration, pH and current density on the mass of the deposit produced was determined. The crystal orientation and morphology of the deposits were evaluated. The behavior of the above two baths are compared.

Key words: Sol-gel technique, amorphous structure, zirconium oxide, ceramic coatings.

Introduction

Ti-6A1-4V is the most widely used titanium alloy in aerospace engineering for its high specific strength in chemical processing and in marine parts for its corrosion resistance and in biomedical engineering for its biomedical compatibility and inertness in the human body. Although Ti-6Al-4V has shown so many good performances in a variety of applications like other titanium alloys it is seriously corroded in some acids such as hydrochloric acid and sulfuric acid, oxidized rapidly at temperature greater than or equal to 1023 K and shows lack of wear resistance to ultra-high-molecular-weight polyethylene (UHMWPE) which is used as a socket in anthroplasty of the hip joint. However, some efforts have been made, such as a) ion implantation of iridium in Ti alloys, anodizing in methanol electrolyte or oxidizing in air to improve its corrosion resistance, and b) plasma-sprayed ion nitriding and diamond coating to increase its wear resistance. On the other hand, ZrO_2 has been considered as a ceramic coatings of high strength and toughness, with good thermal barrier properties, and a lower wear factor to UHMWPE, only 40-60% that of Al_2O_3 and 10-20% that of 316 stainless Steel. Therefore a low-cost process for coating the Ti alloy ZrO_2 is worth exploring [1].

A variety of methods are available for their production, including plasma spraying, chemical vapor deposition (CVD), with sputtering and sol-gel processes to produce ZrO_2 coatings [2].

Formation of ceramic coatings by electrochemical means is a relatively new technique and present several advantages over alternative coating techniques. In the present work, deposition of zirconia (ZrO_2) from an aqueous solution of zirconyl nitrate [$ZrO(NO_3)_2$] and zirconyl chloride [$ZrOCl_2$] were studied and results are presented in this paper.

Experimental

The deposits were obtained on polished titanium of 5 x 1 cm area, the effective plating area being 2x1 cm with due pretreatment. Deposition was carried out from zirconyl nitrate and zirconyl chloride solutions in the concentration range of 0.1 to 0.15 M in the pH range of 2.1-2.3. A controlled power supply was used. The deposits were obtained at current densities ranging from 1- 5 mA/cm² and for a duration of 15 min. The experiments were performed with mild stirring using a magnetic stirrer.

The deposits were dried in air at room temperature. Coating weights were determined by weighing the specimens before and after deposition, with an accuracy of 0.05 mg. Current efficiencies were reported assuming the deposits to be $Zr(OH)_4$ [1]. The deposits were submitted to sintering treatments before XRD and SEM structural studies.

Results and discussions

The thin film and electrolytic deposition of ceramic coatings from an aqueous solution (Sol-gel technique) developed recently enable ZrO_2 coatings of higher thickness after subsequent thermal processing.

The as deposited coatings were transparent. The coating weight and thus the thickness was found to increase with increase of current density and with the duration of coating, Films obtained at low current densities were compact and adherent whereas those deposited above 2 mA/cm² and concentration above 0.125 M were non-adherent, powdery. Also deposits obtained at pH levels above 2.2 exhibited a similar

* Author for correspondence
Email: malathypush@yahoo.com

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nature. It has been reported [2] that the above coatings in the as plated condition exist as $Zr(OH)_4$ which on heat treatment get converted to ZrO_2. The film formation is pH dependant and at low current densities, there is no drastic change in pH at the cathode surface. But at high current densities the H^+ ions generated at the anode neutralize the OH^- ions at the cathode and causes pH reduction [2], affecting film formation. As given in the Table1 in the zirconyl nitrate solution, mass of the film at a constant duration increases up to 0.125 M and above this concentration shows a reduction. This may be due to the increased gel strength in the suspension leading to non-adherent deposits. pH 2.2 is found to be the optimum to produce quality deposits up to 2 mm thickness at 2 mA/cm². At pH 2.3, though the mass of the deposit obtained is higher than at pH 2.1 and 2.3, they were non-adherent. The cathode efficiency calculated as $Zr(OH)_4$ is maximum at 0.125 M pH 2.1 at 3 mA/cm² (Table 1).

In zirconium oxy chloride, the results are slightly different. pH 2.1 is found to be the optimum for deposition at current densities of 1 and 2 mA/cm². Maximum thickness obtained was 2.23mm. Cathode efficiency is maximum at 0.125 M up to 2 mA/cm².

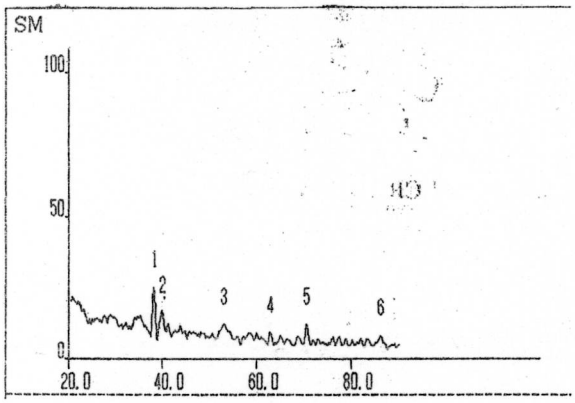

Fig-1. XRD pattern of deposit obtained from zirconyl nitrate

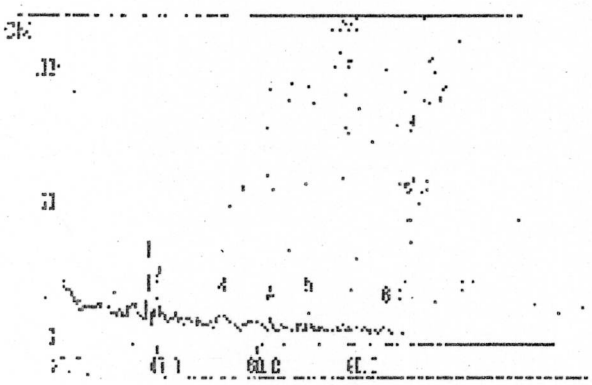

Fig.2. XRD pattern of deposit obtained from zirconyl chloride

XRD analysis of the as plated deposit showed no sharp peaks indicating its amorphous nature. But heat treatment at 680 °C for 10 minutes showed peaks corresponding to ZrO_2. Though the deposits obtained from both solutions generally showed peaks with maximum orientation in the 021 directions, orientations in other directions are different (Figs. 1&2) which along with a shift of the peaks to the positive angles, are the reason for the compact and fine-grained nature of deposits obtained from a chloride solution. The deposits had a mud-cracked structure as shown by the SEM micrographs (Figs. 3 & 4).

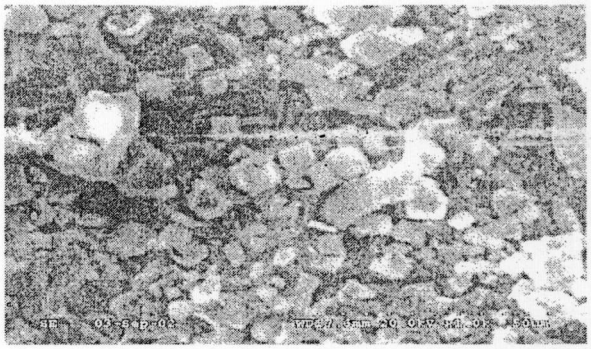

Fig.3. SEM micrograph zro_2 coating from nitrate solution

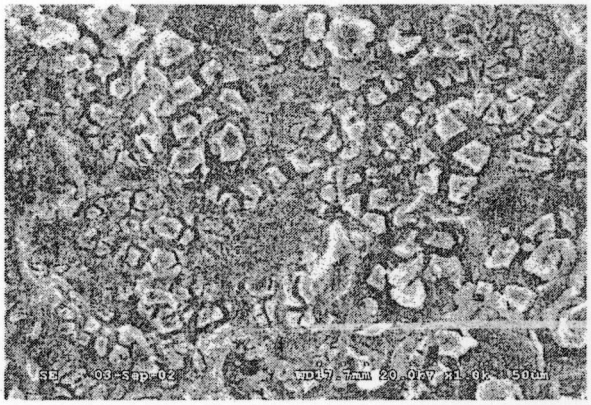

Fig.4. SEM micrograph zro_2 coating from chloride solution

Conclusion

It is possible to obtain adherent ceramic ZrO_2 coatings up to a thickness of 2 mm by adopting electro chemical sol-gel technique. Deposits obtained from chloride solutions are better than those from nitrate solutions.

References

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Table 1. Effect of operating variables on the mass and current efficiency of deposition

pH	c.d. (mA/cm^2)	Concentration (M)											
		0.1				0.125				0.15			
		$ZrO(NO_3)_2$		$ZrOCl_2$		$ZrO(NO3)_2$		$ZrOCl_2$		$ZrO(NO_3)_2$		$ZrOCl_2$	
		Mass mg	C.E %	Mass mg	C.E %	Mass mg	C.E %	Mass mg	C.E %	Mass mg	C.E %	Mass mg	C.E %
2.1	1	0.9	100	1.0	100	1.2	100	2.9	100	0.7	100	0.7	100
	2	1.1	95	1.8	95	1.1	74	2.7	94	1.1	74	1.3	87
	3	1.3	74	1.9	85	1.2	54	0.9	40	1.2	54	1.5	67
	4	1.4	58	1.6	54	1.7	47	0.6	20	1.4	47	2.4	50
	5	1.5	40	1.2	32	2.2	40	0.3	8	1.4	38	0.9	24
2.2	1	0.8	100	1.9	100	1.2	100	1.2	100	0.7	100	0.5	71
	2	1.1	95	2.5	95	2.7	94	0.8	54	0.6	40	0.7	47
	3	1.0	45	1.0	45	2.0	80	0.5	22	0.9	30	1.0	45
	4	1.1	37	0.8	27	1.3	44	0.9	30	0.6	21	1.1	37
	5	0.8	22	0.6	16	1.1	30	1.6	43	0.8	20	1.2	32
2.3	1	1.0	100	1.0	100	1.1	100	1.3	100	1.7	100	1.6	100
	2	1.3	87	1.8	94	1.3	87	2.3	95	1.6	95	1.7	95
	3	0.9	40	1.9	85	1.9	85	1.9	85	0.8	36	1.9	85
	4	0.7	24	1.6	54	0.6	20	0.3	10	0.8	27	1.9	64
	5	0.3	8	1.2	32	0.1	2	0.2	5	0.5	13	1.3	35

Bio-data of Dr.(Mrs.) Malathy Pushpavanam
Best Electroplater Award for the year 2000

THE SOCIETY FOR ADVANCMENT OF ELECTROCHEMICAL SCIENCE AND TECHNOLOGY AND THE METAL FINISHERS ASSOCIATION OF INDIA, MUMBAI (SPONSOR) are pleased to honor **Dr. (Mrs.) MALATHY PUSHPAVANAM**, Scientist, Central Electrochemical Research Institute, Karaikudi with the prestigious **BEST ELECTROPLATER AWARD** for the year 2000.

Born on 21st January 1948, **Dr. (Mrs.) MALATHY PUSHPAVANAM** finished her graduation in Madras University and joined the Industrial Metal Finishing Division of Central Electrochemical Research Institute in 1968 as Senior Laboratory Assistant. She qualified herself with the Associate ship of the institution of Chemists, Calcutta and then with the doctorate degree in Punjab University, Chandigarh on the topic "Studies on the Characterization of Electrodeposited Nickel alloys and Composites" in the year 1989. She has grown up with the organization, rose up to the level of a senior scientist and now heading the group of Alloys and Composite Plating, Platinum Metals' Plating, Heavy metal deposition and Plating on Difficult to Plate metals.