Int. Journal of Refractory Metals and Hard Materials 50 (2015) 204–209

Contents lists available at ScienceDirect

Int. Journal of Refractory Metals and Hard Materials

journal homepage: www.elsevier.com/locate/IJRMHM

Growth mechanism and mechanical property of laminar iridium coating by electrodeposition

Yongle Huang, Shuxin Bai *, Hong Zhang, Yicong Ye

Department of Material Science and Engineering, College of Aerospace Science and Engineering, National University of Defense Technology, Changsha 410073, PR China

ARTICLE INFO

Article history:
Received 12 December 2014
Accepted 20 January 2015
Available online 21 January 2015

Keywords:
Iridium coating
Mechanical property
Heat treatment
Electrodeposition
Molten salts

ABSTRACT

Iridium coatings were prepared on rhenium coated graphite by electrodeposition. The Ir coatings were annealed at 1250 °C, 1600 °C and 1950 °C for 7.5 h, respectively. Growth mechanism and mechanical properties of the Ir coatings were investigated. Results showed that the as-received Ir coatings had thickness of about 0.25 mm and characterized as laminar columnar grain structure, which resulted from using higher and lower current densities (−50 mA/cm^2 and −20 mA/cm^2) alternately. Annealing temperature affected mechanical properties of the Ir coating by changing residual stress, defects and grain size of the coating. The average tensile strength of the as-received, 1250 °C-annealed, 1600 °C-annealed, 1950 °C-annealed (in vacuum) Ir coating and 1950 °C-annealed (in hydrogen) was about 250 MPa, 270 MPa, 234 MPa, 117 MPa and 91 MPa respectively.

1. Introduction

Reliable materials are urgently needed for the requirement for high temperatures, high flow rate and oxidative erosion environment encountered in rocket propulsion and aerodynamic heating reentry applications [1,2]. Iridium (Ir) is considered as one of the most promising oxidation resistance materials for high temperature applications because of its high melting points, good physical and mechanical properties [3,4], low oxygen and carbon permeability up to 2100 °C [5,6], and good chemical compatibility with refractory metal oxides, carbides and borides [7]. Ir and its alloys have been used as crucible materials for the growth of single crystals in industries. Ir coated refractory metals and carbon structural materials have been used for liquid rocket engines, leading edges and noses of hypersonic aircraft [8–12].

Ir coatings have been prepared by many kinds of methods, such as metal organic chemical vapor deposition (MOCVD), sputtering deposition (SP), electrodeposition (ED) and double-glow plasma deposition (DPD) [13–19]. Among these methods, ED is considered as one of the most efficient and high-quality methods for fabricating uniform, dense and thick Ir coating on complex-shaped components [20–22].

Much attention has been focused on the effects of various preparation parameters on the morphology and microstructure of Ir coating and determined some properties of Ir coating, including density, purity, hardness and oxidation resistance [23–27]. Growth mechanism of laminar Ir coatings and effects of high temperature heat treatment on the mechanical properties is very crucial to its applications. In the present work, thick Ir coatings were prepared on rhenium (Re) coated graphite by electrodeposition from molten chloride salts by oft-repeated two-segment cathodic current (shown in Section 2.1). The Ir coatings were annealed at 1250 °C, 1600 °C and 1950 °C for 7.5 h, respectively. The growth mechanism and effects of high temperature heat treatment on the mechanical properties of Ir coatings were investigated.

2. Experimental

2.1. Preparation of Ir coatings

The apparatus for electrodeposition of Ir coating under inert atmosphere protection has been previously described [28]. Graphite (8710, SGL Carbon Company, Germany) were used as substrates. Then a Re coating was prepared on graphite specimen as interlayer by chemical vapor deposition (CVD). The details of the CVD process were reported in our previous work [29]. Before electrodeposition, to remove entrapped gasses and impurity from the substrates, Re/C specimens were carefully ultrasonically cleaned in acetone and annealed at 1300 °C for 10 min in argon atmosphere by an induction heater. The Re/C specimens were used as the cathode and immersed into the molten salt during electrodeposition. A cylinder graphite crucible storing the electrolyte salts was used as the anode, which was degassed at 1500 °C for 1 h in a vacuum furnace before used. A ternary eutectic molten salt of NaCl–KCl–CsCl (29.8, 29.8 and 40.4 mol%, respectively) used for making electrolyte bath were dried at 150 °C in a vacuum chamber for 5 h before being mixed and melted. Ir ions were introduced by adding $IrCl_3$ (purity: 99.99%, Shaanxi Kaida Chemical Engineering Co., Ltd) directly into the melting salts. The oft-repeated two-segment cathodic current, namely a higher current density (50 mA/cm^2) segment (Segment I) that lasted 300 s and a lower current density (25 mA/cm^2) segment

* Corresponding author.
E-mail address: NUDT_MSE_501@163.com (S. Bai).

http://dx.doi.org/10.1016/j.ijrmhm.2015.01.009
0263-4368/

(Segment II) that lasted several hours was alternately carried out during electrodeposition. In a two-segment, a higher and lower current density was contained. Five such two-segment current cycles were executed totally as shown in Table 1. Other electrodeposition parameters were listed in Table 2.

2.2. Heat treatment

The as-received Ir coatings on the specimens were cut into 50 × 3 mm strips by wire-electrode cutting. The Ir coating was separated from the graphite substrates by using aqua regia to erode Re interlayer between them. The Ir strips were carefully ultrasonically cleaned in acetone for 15 min and dried at 150 °C in a vacuum chamber for 5 h. The high temperature heat treatment was carried out in tungsten sheet furnace. Groups of specimens and experiment parameters were listed in Table 3. In each groups, three specimens had been annealed and tested. The weight of the Ir coating specimens before and after heat treatment was measured by electronic balance (AB104-N, Switzerland Mettler-Toledo Group Ltd.)

2.3. Tensile and micro-hardness tests

The tensile strength and elongation of the Ir coatings before and after heat treatment was examined in a material testing machine (GMT9100, Shang Hai Yi Qiang Instruments Inc.). Shown as the schematic diagram (Fig. 1), two ends of the Ir strips were glued by thick aluminum (Al) boards for chucking during test process. The parallel distance L_c between the two chucks was 30 mm. The tensile test was executed at a speed of 0.5 mm/min in room temperature. The gauge distance L_0 of plastic deformation zone was 9.74 mm (~$11.3S_0$½). The micro-hardness (Vickers hardness) of the Ir coating was measured by micro-hardness tester (HXD-1000TC, Shanghai Optical Instruments Inc.) with 50 g of loading for 15 s.

2.4. Characterization

The surface and fracture face morphologies of the Ir coating was observed by Hitachi S-4800 scanning electron microscope (SEM). The phase identification and growth direction of the Ir coating were determined by X-ray diffraction (XRD, Rigaku D/Max 2550VB+) using Ni-filtered Cu Kα radiation at a scanning rate of 5°/min and scanning from 35° to 85°of 2θ.

3. Results and discussion

3.1. Growth mechanism of laminar and thick Ir coating

Fig. 2a showed fracture surface morphology of the as-received Ir coating. The Ir coating consisted of about five columnar layers from the bottom (side adjacent to graphite substrate) to the top with blurred inter-layer interface. Total thickness of the coating was about 250 μm. The thickness of each layer was basically coincided with theoretical thickness calculated by Faraday's law through the quantum of electrons transferring in each two-segment current cycle (list in Table 1). It demonstrated that every columnar layer might be corresponding to one cycle of the two-segment cathodic current carried out during electrodeposition.

Fig. 2b showed the top side surface of the as-received Ir coating. The Ir coating was continuous and dense without any visible defects. Comparatively, the Ir coating on the bottom side was smooth and homogeneous, but discontinuous with amounts of pinholes (Fig. 2c). These pinholes might be left behind between the boundaries due to the "inland growth" of Ir grains at the beginning of electrodeposition. Ir grains on the top side were quite coarse, but ultrafine on the bottom side. According to the two-segment cathodic current carried out, the coarse Ir grains on the top side were deposited under the lower current density (segment I). The ultrafine Ir grains on the bottom side were corresponding to the higher current density segment (segment II). Higher current density would result in larger over-potential in electrode, which promoted nucleation of Ir grains in the coating. Conversely, small over-potential in electrode promoted extensive growth of Ir grains, which resulted thick and columnar grain structure in Ir coating. Therefore, laminar columnar structure of Ir coating was received by using the oft-repeated two-segment cathodic current. The thickness of each layer was determined by the quantum of electrons transferring at cathode in one two-segment current cycle.

The Ir coating with the laminar columnar grain structure would have better oxidation resistance and mechanical properties than monolayer columnar grain structure Ir coating. On one hand it increased the diffusion distance of in-diffused oxygen and out-diffused rhenium; on the other hand closely bonded interfaces between layers would also improve mechanical properties of the coating.

Table 1
The oft-repeated two-segment cathodic currents carried out during electrodeposition.

Cycles	Segments	j/mA·cm^{-2}	Time/s	Theory thickness/μm
1	Segment I	50	300	31
	Segment II	25	3600	
2	Segment I	50	300	44
	Segment II	25	5400	
3	Segment I	50	300	70
	Segment II	25	9000	
4	Segment I	50	300	57
	Segment II	25	7200	
5	Segment I	50	300	83
	Segment II	25	10,800	

Table 2
Electrodeposition parameters of iridium coating.

Deposition temperature	500–700 °C
Content of Ir^{3+}	1.9 at.%
Atmosphere	Air
Growth rate	~25 μm/h
Deposition time	1~2 h

3.2. Heat treatment of Ir coating

Fig. 3 showed the surface and fracture face morphologies of the Ir coatings after being annealed at various temperatures for 7.5 h. The top side surface of the Ir coating after being annealed in hydrogen atmosphere at 1950 °C was turned to be much smoother. But it became discontinuous and incompact with large amount of grooves and pores at grain boundaries (Fig. 3a). Ir grain boundaries were a little sunk and Ir grain size was increased distinctly to about 100 μm. Thickness of the annealed Ir coating remained to be about 250 μm with five columnar layers. The thickness of each columnar layer was basically unchanged, but inter-layer interfaces turned to be much clearer. Some pores were found at the interface. The annealed Ir coating kept relatively compact without any penetrating defects. After fracture, some fracture steps were also observed at the interfaces. Some V-grooves with depth of

Table 3
Groups of heat treatment experiments.

Groups	Temperature/K	Atmosphere	Time/h
I	The as-prepared Ir coatings		
II	1950 °C	Hydrogen, 1 atm	7.5
III	1950 °C	Vacuum, 10^{-3} Pa	7.5
IV	1600 °C	Vacuum, 10^{-3} Pa	7.5
V	1250 °C	Vacuum, 10^{-3} Pa	7.5