Vacuum 154 (2018) 227–234

Contents lists available at ScienceDirect

Vacuum

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

Study of thermal ageing effects on Rh coating's mechanical performance upon CuCrZr substrate through modeling and experimental methods

Z.X. Chen[a,b,*], J. Hillairet[a], V. Turq[b], Y.T. Song[c], R. Laloo[b], K. Vulliez[d], J.M. Bernard[a], Q.X. Yang[c], C. Hernandez[a], L. Ferreira[e], F. Fesquet[e]

[a] CEA, IRFM, F-13108, Saint-Paul-Lez-Durance, France
[b] Institut Carnot CIRIMAT, UMR CNRS-UPS-INP 5085, Université Paul-Sabatier, 118 Route de Narbonne, 31062, Toulouse Cedex 9, France
[c] Institute of Plasma Physics, CAS, Hefei, Anhui, 230031, China
[d] Laboratoire d'étanchéité, DEN/DTEC/SDTC, CEA, 2 Rue James Watt, 26700, Pierrelatte, France
[e] CERN, Geneva, Switzerland

ARTICLE INFO

Keywords:
Rh coating
CuCrZr
Thermal stress
Cracking
Hardness
Adhesion

ABSTRACT

Rhodium (Rh) coating on CuCrZr substrate is a promising material option for optical, structural and electrical applications on nuclear fusion reactors. For these applications, Rh coated CuCrZr components subject to long time of thermal ageing due to pre-treatment or normal operation condition. In this paper, both finite element method (FEM) and experimental method were applied to investigate the effects of thermal ageing on mechanical performance of Rh coating after 250 °C, 500 h baking in vacuum. Based on FEM analysis, thermal stresses which concentrate at Rh coating interface is the main source of cracking, and such stresses can be minimized efficiently by introducing a 0.5 μm Au interlayer into the coating layer structure. According to thermal ageing experiments, through-thickness cracking in the Rh coating due to thermal stress releasing and voids generated at the Rh bonding interface caused by Kirkendall effect were the main micro-structure changes in the coating system. The solid-solution hardening caused by significant Cu diffusion into Rh is the dominant factor that affected the Rh coating's hardness. The existing of large amount of cracks in the Rh coating and voids at the Rh coating interface deteriorated the adhesion performance of Rh on CuCrZr substrate by 30%.

1. Introduction

Metallic rhodium provides the unique combination of excellent physical and chemical properties especially in electrical conductivity, hardness, optical reflectance and wear resistance. Due to its good properties, Rh has wide industrial applications on electronics, electrical contacts, optic equipment and medical implants as well [1]. As a noble metal, it is costly to use Rh as bulk material to manufacture products, and instead, depositing it as a functional film on suitably selected base materials is a common industrial approach. Rh coatings are typically deposited by electroplating, physical vapor deposition, or chemical vapor deposition techniques [2].

Rh deposition by magnetron sputtering was explored and studied for the application as a coating material candidate for the International Thermonuclear Experimental Reactor (ITER) first mirror diagnostic, which sustains repetitive thermal stress load [3–7]. In these studies, the attempt of applying Rh thin coating (200 nm) on stainless steel 304 L, molybdenum and Cu was performed and their failure mechanisms were investigated. According to the results, Rh on 304 L showed much better coating attachment performance than on Cu. And from the micro-scratch tests, the critical load of Rh on Cu is only about 1/4 of the critical load of Rh on 304 L. Compared with stainless steel, Cu and Cu alloys have much better thermal and electrical properties which are appropriate to be used on electrical or thermal handling applications such as electrical contact. In addition, Rh coating can be plated as protective coating which prevents its substrates from wear. On the Large Hadron Collider (LHC) accelerator, Rh coatings on Cu and CuBe (C17410) were evaluated based on their electrical performance for sliding RF contact application [8–10]. On ITER tokamak, RF sliding contacts [11–13] are being developed on which Rh is expected to be electroplated on the CuCrZr substrate to improve its wear and corrosion resistance.

For fusion reactor applications, the Rh coatings being applied are working under high or ultrahigh vacuum [14,15], and long duration of high temperature baking around 250 °C (with a slow heating rate about 5 °C/h) is mandatory for outgassing [16,17]. Although Rh coatings' mechanical performance on different substrates were researched and introduced in other literature [3,5], the effects of 250 °C thermal ageing

* Corresponding author. CEA, IRFM, F-13108, Saint-Paul-Lez-Durance, France.
E-mail address: zhaoxi.chen@cea.fr (Z.X. Chen).

https://doi.org/10.1016/j.vacuum.2018.05.018
Received 15 April 2018; Received in revised form 12 May 2018; Accepted 14 May 2018

on the Rh coatings' properties and adhesion performance were not detailed studied, which is very important to evaluate the Rh coatings' life time used on such machines as wear protective coatings. The purposes of this paper are to investigate the thermal ageing effects on the Rh electroplating upon CuCrZr substrate by using finite element method (FEM) as well as experimental method, and to understand the mechanisms of crack generation, hardness transition and adhesion strength variation caused by thermal ageing process.

2. Coating design and thermal stress modeling

The mechanical integrity of a coating material depends on the residual stresses which come from four principal sources: growth stresses during coating formation, geometric constrains, service stresses and thermal stresses [18]. Thermal stresses are induced during the baking and cooling periods by the uniform temperature distribution of the structure and the thermal expansion mismatch between the coating and the substrate [19,20]. Considering the relative small thickness of the Rh coating to the massive CuCrZr substrate and the low temperature transition rates during heating and cooling processes, at every moment the temperature on the components can be regarded as steady-state, and there is no significant temperature gradient exists between Rh coating and its substrate. Thus, the difference of coefficient of thermal expansion (CTE) between materials is the major source of thermal stresses. Unlike functional Rh coatings used for optical applications, to be used as wear resisting coatings, larger thickness is required. The increase of the coating thickness can decrease the bonding strength and increase the residual stress [21]. Therefore, for thick Rh coatings, thermal stresses should be evaluated carefully.

Instead of depositing the coating materials directly on the substrates, applying interlayers can obviously reduce the residual stresses by reducing the mismatch of CTE between coating and its substrate [22]. In addition, for rigid coating and substrate, applying of a relative soft interlayer can relax thermal stresses through phenomena of ductile, creep and plasticity [23]. For the electroplating point of view, non-precious metals can be properly plated only after pre-plating of Ni or Au interlayer to avoid the substrate corrosion in the high acidity of Rh electrolyte [1], and the good adhesion of Rh on Au had been approved [24]. As shown in Table 1, Au is a suitable interlayer coating candidate to improve the thermal stresses in the Rh coating.

2.1. Analysis model and boundary conditions

Numerical simulation of the thermal stresses generated in the Rh coating during baking period (heating-up and cooling) and the effects of introducing Au interlayer were simulated by using ANSYS FEM code. The thickness of the Rh coating was fixed as 3 μm and the interlayer of Au was modeled as 0.5 μm. The case without interlayer can be simulated by changing the interlayer material from Au to CuCrZr. Although the thickness of the CuCrZr substrate was defined as 20 μm, the substrate is thick enough in comparison to the coating layers to reveal the true mechanical behaviors. Transversal cross-section of the coatings was modeled in a 2-D approach as shown in Fig. 1. There are several assumptions in the finite element (FE) analysis model: the model is assumed to be perfect elastic bodies without plastic deformation occurring; the coating interfaces are perfect bonding with low thermal contact resistance; the temperature on the whole model is uniform without temperature gradient existing and the whole model was stress free after electroplating at room temperature (i.e., 25 °C).

Table 1
Main material properties of Rh, CuCrZr and Au at room temperature.

Property	Material		
	Rh	CuCrZr	Au
CTE (× 10^{-6}/K)	8.2	16.7	14.2
Young's Modulus (GPa)	372	127.5	76.6
Poisson's Ratio	0.26	0.33	0.42

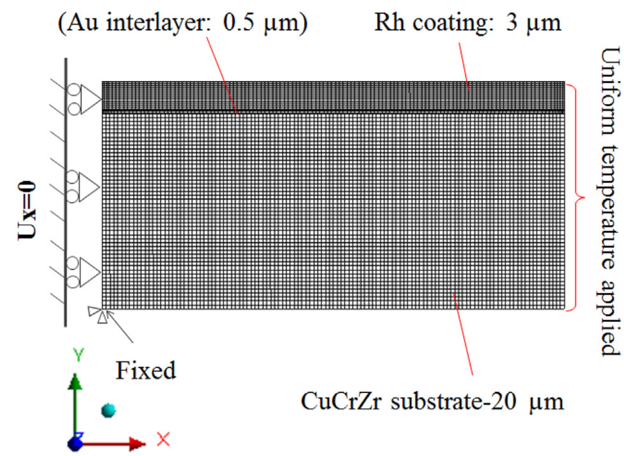

Fig. 1. FE modeling and boundary conditions.

In order to improve analysis precision, mapped meshing was used to generate full quadrilateral-shaped elements and fine mesh was applied on the two thin coatings to avoid high stress concentration. The displacement of the model's left edges was constrained in X direction and free in Y direction and the node located at the bottom left corner was fixed without any movements permitted. Thermal loads were applied on the model by setting the reference temperature as 25 °C and body uniform temperature from 25 °C to 250 °C to mimic the heating-up period (the same stresses results as cooling period from 250 °C to 25 °C).

2.2. Von-Mises stress analysis result

Static structural analyses were performed and the maximum Von-Mises stresses on the model under different temperature loads as well as with or without Au interlayer were plotted in Fig. 2 (a). The maximum thermal stress is almost linearly increased with the increase of the baking temperature. When baking temperature rises to its peak value of 250 °C, the maximum thermal stress in the Rh layer without Au interlayer is about 333 MPa and this value can be reduced significantly by 44 MPa if a 0.5 μm Au interlayer applied. From Fig.2 (c) and (d), it can be seen that the peak stresses occurred at the corner and high tensile stress appears only in Rh layer near the bonding interface with Au or CuCrZr. Fig. 2 (b) shows the distribution of thermal stress through the thickness of the coating and substrate at the right edge. The stress distributions for the cases with and without Au interlayer are similar, and the tensile stress in the Rh coating increases with the depth increase and this stress turns to compressive stress in the Au and CuCrZr layers with a sudden value decrease. The yield stress of Rh was reported in Ref. [25], which showed that the yield stress of Rh at room temperature is 67 MPa. So, even though Au interlayer is applied, yield phenomenon of Rh layer especially at the coating interface would be inevitable. And large tensile stress in the Rh layer is prone to generate cracks.

2.3. Shear stress analysis result

The coating failure mechanism has a close relationship with the shear stress and the shear stress reveals the adhesion strength of the coating [26]. Spallation of the coating can occur if the shear stress at the bonding interface is higher than the bonding strength. The shear stress distribution of Rh coating at 250 °C along X-direction at different depth with and without Au interlayer was studied and the results are shown in Fig. 3. As free surface, the shear stresses at the top surfaces are very low. Both for the Rh coatings with and without Au interlayer, when the depth getting deeper, the shear stress increases accordingly.