Surface & Coatings Technology 344 (2018) 102–110

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Vacuum heat treatment mechanisms promoting the adhesion strength of thermally sprayed metallic coatings

Guo-Hui Meng, Bang-Yan Zhang, Hong Liu*, Guan-Jun Yang*, Tong Xu, Cheng-Xin Li, Chang-Jiu Li

State Key Laboratory for Mechanical Behavior of Materials, School of Materials Science and Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, PR China

ARTICLE INFO

Keywords:
Thermal spray
Vacuum heat treatment
Adhesion strength
Oxide film
Diffusion
Thermodynamic model

ABSTRACT

In this study, the mechanisms responsible for enhancing the adhesion strength of thermally sprayed metallic coatings subjected to vacuum heat treatment were investigated using atmospheric plasma sprayed (APS) CoNiCrAlY coatings as an example. The formation of metallurgical bonding between the coating and the substrate, which determined the increase in the adhesion strength of the coatings, was studied by analyzing the effect of morphological changes of the oxide film in the coating. The results showed that during the vacuum heat treatment process, the oxide film formed during the coating deposition gradually broke down and subsequently shrank into round-shaped oxide inclusions. After vacuum heat treatment, the adhesion strength of the coating improved significantly. The increase in the adhesion strength was caused by the formation of metallurgical bonding between the coating and the substrate. However, the prerequisite for the formation of metallurgical bonding was that the oxide film had to break during the vacuum heat treatment process. A thermodynamic 2D model based on the thermal grooving theory was proposed to explore the essential conditions for the breaking and shrinking of the oxide film. The results predicted by the 2D model and the experimental results were in good agreement with each other and indicated that at a given temperature, the breaking of the oxide film is directly related to its thickness.

1. Introduction

In order to ensure that the mechanical components used in harsh environments have enough service life, metallic protective coatings are usually deposited on their surfaces [1–4]. Metallic protective coatings can assist in maintaining the mechanical properties of the components while improving the resistance of the structural parts to external environmental damage [1]. In general, the successful application of metallic protective coatings for engineering usage depends strongly on the quality of adhesion between the coating and the substrate [5]. Low quality adhesion could lead to premature failure of the coating, which results in the structural parts being exposed to harsh environments, which in turn can cause serious damage [6].

Thermal spraying is a well-established technology and has been widely employed to deposit different types of metallic protective coatings [7]. In most cases, the adhesion between the thermal sprayed coating and substrate is attributed to the mechanical interlocking [8,9]. In addition, the interaction (adhesive interaction (Van der Waals forces) and/or metallurgical interaction (metallurgical bonding)) between the first splat and the substrate also contributes to the adhesion [5,8,10]. However, it must be noted that in the case of thermally sprayed metallic coatings, the first splat does not fully cover the substrate. The contact areas between the bottom of the first splat and the substrate are sometimes called welding points or active zones, which account for just about 20% to 30% of the entire splat area [8,11]. Moreover, in the contact zone, although metallurgical bonding is a strong form of bonding, its proportion in the contact area is very small [5,10]. In general, pores occupied most of the area between the splats and the substrate [12]. As pores can become the sources for cracks and act as channels for crack propagation, the adhesion strength of thermally sprayed metallic coatings is usually low.

Because adhesion strength determines the ability of the coating to resist spalling during service, much importance is attached to improving the adhesion strength of metallic coatings deposited by thermal spraying [3,6,13]. It is worth mentioning that vacuum heat treatment is widely used to improve the quality of metallic coatings [8,9]. One of the functions of vacuum heat treatment is to enhance the adhesion strength of the coating. Richard et al. [6] reported that during vacuum heat treatment, the metallic coating contacted the metallic substrate, leading to a diffusion of elements between the two components. This

---

* Corresponding authors.
E-mail addresses: hongliu@mail.xjtu.edu.cn (H. Liu), ygj@mail.xjtu.edu.cn (G.-J. Yang).

https://doi.org/10.1016/j.surfcoat.2018.03.010
Received 26 October 2017; Received in revised form 3 March 2018; Accepted 6 March 2018

results in a decrease in the porosity and an increase in the proportion of metallurgical bonding in the active zone. Therefore, the adhesion strength of a coating can be improved by vacuum heat treatment. However, it is worthwhile to note that during the coating deposition process in ambient conditions, the sprayed particles inevitably come into contact with oxygen during flight in the flame jet and eventually a layer of metal oxide is formed around the molten particles [14]. Even in the case of metallic coatings deposited by vacuum plasma spray, it has been shown that the molten particles reacted with the residual oxygen in the vacuum device and formed an oxide layer, a few tens of nanometers thick, on the surface of the splat [2]. Evans et al. [15] confirmed that the presence of an oxide film prevents the diffusion of metallic elements and results in the single splat coated by the oxide film becoming an isolated diffusion core unit. In other words, if an oxide film exists on the splat surface, it is difficult to enhance metallurgical bonding between the coating and the substrate via vacuum heat treatment. However, a large number of studies have reported that the adhesion strength of the metallic coatings deposited by thermal spraying improved significantly after vacuum heat treatment [6,8,9]. There are differences between the theoretical and experimental results. Further research is therefore required to understand the root causes for such differences.

After vacuum heat treatment, the adhesion strength of the metallic coatings changes significantly. The answer to this question may be that the oxide film, which acts as a barrier to the diffusion of metallic elements, undergoes changes during the vacuum heat treatment process. Therefore, it is necessary to investigate this issue by focusing on the changes in the diffusion barrier. However, in the case of a coating deposited in a low oxygen atmosphere (such as vacuum plasma spray), the oxide film may be too thin to observe the changes in the diffusion barrier. On the other hand, as a metallic protective coating with good resistance to high temperature corrosion and oxidation, CoNiCrAlY coatings deposited by different thermal spray processes have been widely studied and many reports focused on improving the adhesion strength of these coatings by vacuum heat treatment [8,9,16,17]. Therefore, in this study, considering atmospheric plasma-sprayed CoNiCrAlY coatings as an example, the changes in the diffusion barrier of oxide film during the vacuum heat treatment process were studied. It is found that the morphology of the oxide film changed significantly during the heat treatment process. With an increase in the heat treatment time, the oxide film gradually broke down and shrank into round-shaped oxide inclusions. After the oxide film broke down, metallurgical bonding between the coating and the substrate was enhanced, which led to an increase in the adhesion strength of the coating.

2. Experimental procedures

2.1. Preparation of coatings

First of all, disc-shaped specimens, 25.4 mm in diameter and 3 mm in thickness, were cut from a cylindrical rod made up of a nickel-based superalloy Inconel-738 using spark erosion. The nominal composition (in wt%) of this superalloy (NCS) was listed in Table 1. Because this study focused mainly on the reason behind the metallurgical bonding between the coating and the substrate during vacuum heat treatment and the effect of metallurgical bonding alone on the adhesion strength of the coating, it was necessary to eliminate any interference by other factors. Although roughened substrates are used in practice, heat treatment might alter the mechanical interlocking between the coating and the substrate, thus affecting the improvement in the adhesion strength of the coating due to metallurgical bonding. Therefore, it was necessary to use mirror-polished substrates. This approach was followed in a large number of investigative efforts on the morphology of single splats and the bonding between the splats and polished substrates [10,18–20]. At the same time, it is easier to observe the changes in the bonding between the coating and substrate using polished substrates. In summary, we chose a polished alloy as the substrate. Therefore, prior to coating deposition, the substrate was prepared by successive grinding and polishing. Grinding was carried out using 1200 grit SiC abrasive paper. Polishing was performed using a paste of 1.5 μm and 0.25 μm diamond grains. After grinding and polishing, these specimens were thoroughly cleaned ultrasonically with isopropanol and dried by blowing with compressed nitrogen gas.

A commercial spraying powder of CoNiCrAlY (Amdry 9951, Oerlikon Metco, Switzerland) was selected for coating deposition. This powder was produced by argon atomization and contained spherical particles with a mean particle size of 25.8 μm ($d_{10} = 12.9$ μm and $d_{90} = 38.6$ μm). The nominal composition (in wt%) of this powder (NCP) was listed in Table 2. Later, a 350 μm-thick CoNiCrAlY coating was deposited on the as prepared superalloy surface using a commercial atmospheric plasma spraying system (GP-80, Jiu Jiang, China). The torch used for coating deposition was a machine-mount torch (9MBM, Oerlikon Metco, Switzerland). During coating deposition, 12 passes were completed to achieve the thickness of 350 μm. The specific spray conditions were listed in Table 3.

2.2. Vacuum heat treatment

Vacuum heat treatment experiments were performed in an industrial vacuum furnace (SBF 966H, EXEMOO, China) at 1373 K (a temperature commonly used in the vacuum heat treatment of the thermal sprayed MCrAlY bond coat [21,22]). The specimens were placed in an annealed alumina crucible and transported to the hot zone of the furnace. The coating/superalloy system was then heated to 1373 K at a heating rate of 4 K/min when the furnace pressure was below 1×10^{-3} Pa. The exposure time of different specimens was varied between 4 h and 10 h at 1373 K. After the heat treatment, the specimens were allowed to cool in vacuum to the ambient temperature at a cooling rate of 4 K/min.

2.3. Characterization

The type of bonding (mechanical bonding or metallurgical bonding) between the coating and substrate has a great influence on the adhesion strength of the coating and usually the adhesion strength of a coating can be qualitatively characterized by the type of bonding [3,8]. Therefore, it is necessary to characterize the type of bonding of the coating-substrate interface before and after vacuum heat treatment. Electron backscattered diffraction (EBSD) is a commonly used method to characterize the grain boundary and grain orientation of materials, based on which the type of bonding between the coating and substrate can be judged. In the case of thermally sprayed metallic coatings, in the active zones, metallurgical bonding between the as-sprayed coating and the substrate is mainly due to the melting of the substrate [3,8]. After

Table 1
EDS test results (in wt%) of the substrate.

Elements	Ni	Cr	Co	Al	Ti	W	Mo	Ta	Nb	C	Zr	B
NCS	61.57	16	8.5	3.5	3.25	2.6	1.75	1.75	0.8	0.17	0.1	0.01
S1	62.16	15.9	8.3	3.4	3.31	2.5	1.73	1.71	0.7	0.18	0.1	0.01
S2	62.06	15.9	8.4	3.4	3.18	2.5	1.66	1.83	0.8	0.16	0.1	0.01