Surface & Coatings Technology 331 (2017) 153–162

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Embedment of eutectic tungsten carbides in arc sprayed steel coatings

Wolfgang Tillmann, Leif Hagen*, David Kokalj

Institute of Materials Engineering, TU Dortmund University, Leonhard-Euler-Straße 2, 44227 Dortmund, Germany

ARTICLE INFO

Keywords:
Arc spraying
Tungsten carbide
External powder injection
Steel coatings

ABSTRACT

Tungsten carbide reinforced deposits have already evolved into a predominant coating system in order to protect stressed surfaces against wear. Among thermal spraying processes, due to a high deposition rate, arc spraying is a promising process to manufacture cost-saving, wear resistant coatings. However, inherent process characteristics prevailing in arc spraying as well as the utilization of tungsten carbides, as a filling for cored wires, could lead to undesirable phase evolutions, which in turn provoke the degradation of the mechanical properties. The embedment of tungsten carbides into the surrounding metallic matrix is affected by metallurgical interactions with molten spray particles.

Within the scope of this study, an external injection of tungsten carbides was applied in order to analyze the embedment of tungsten carbides in arc sprayed low alloyed steel. Accordingly, metallographic investigations were carried out, which address the reactive layer at the interface of embedded tungsten carbides to the surrounded iron-based matrix. Microstructural characteristics such as mechanical properties and phase composition were scrutinized by means of nanoindentation, energy dispersive X-ray spectroscopy, and X-ray diffraction, respectively. It was found that the embedment of tungsten carbides, which have been externally injected into the arc burning zone, differs from that obtained from deposits produced with the use of cored wire with tungsten carbide as filling. Thus, externally injected tungsten carbides are less inclined to form eta carbides due to dissolution, which again results in differences in the mechanical properties across the reactive layer.

1. Introduction

The twin wire arc spraying (TWAS) process is a time saving [1] and energy efficient [2] technique, mainly used in surface refurbishments and maintenance applications [3]. Nevertheless, TWAS has the ability to deposit wear and corrosion resistant coatings in a simple and cost saving way due to the use of compressed air as atomization gas, and hard particle reinforced cored wires as feedstock, respectively.

Within the field of wear protection, arc sprayed coatings, produced by utilizing cored wires with hard particle as a filling, are widely used to enhance the tribological and mechanical characteristics of surfaces. Due to their outstanding properties, tungsten carbide reinforced arc sprayed coatings are appropriate to protect stressed surfaces against wear. In terms of arc sprayed coatings, only few studies have discussed the use of tungsten carbide reinforced feedstock materials such as iron-based (FeCSiMn-WC/W_2C, Fe_3Al-WC, Fe-FeB-WC) [4–8] as well as nickel based alloys ((NiCrBSi, NiBSi)-WC/W_2C, Ni-(WC-Co)) [3,9,10]. According to studies on tungsten carbide reinforced Fe-based arc sprayed coatings, a major objective was the focus on the tribological behavior [4,6–8]. It was found that a fine lamellar coating structure, provided by utilizing fine-grain hard material fillings, can lead to enhanced tribological coating characteristics [6].

With respects to the feedstock, Ni-based and Co-based coatings cause some health and safety issues. Ni-based alloys are allergenic, labelled as suspect carcinogenic agents [11], and classed as hazardous powder materials (hazard statement according to the European Commission regulation EC 790/2009) [12]. Regarding the WC–Co feedstock, it is reported that the materials are also toxic when inhaled [13]. Moreover, the feedstock is listed in the “Report on Carcinogens” [14]. In terms of the compatibility of thermal spray coatings in the food production technology (according to EU and PDA standards), coatings containing Ni- and Co- might fail to meet the specific requirements within this field such as strict limitations concerning the contamination of the products with harmful or even toxic elements [15]. Regarding thermally sprayed coatings, Fe-based alloys have proven to be less hazardous when compared to Ni- and Co-based alloys. However, Fe-based alloys are known to be less corrosion resistant compared to Ni- and Co-based alloys. Over the last decades, it was already demonstrated that Fe-based amorphous coatings provide a corrosion resistance comparable to that of high-performance alloys such as Ni-based alloys [16]. As a result, some Fe-based materials already replace more expensive Co- or Ni-based alloys in various industry applications where the components are subjected to corrosion and wear [17]. It can be stated

---

* Corresponding author.
E-mail addresses: wolfgang.tillmann@tu-dortmund.de (W. Tillmann), leif.hagen@tu-dortmund.de (L. Hagen), david.kokalj@tu-dortmund.de (D. Kokalj).

http://dx.doi.org/10.1016/j.surfcoat.2017.10.044
Received 24 June 2017; Received in revised form 13 October 2017; Accepted 14 October 2017

that tungsten carbide reinforced Fe-based Metal Matrix Composites (MMCs) represent an environmentally friendly alternative.

By means of arc spraying, tungsten carbide reinforced coatings are manufactured exclusively by using of cored wires. These cored wires mainly consist of a metallic (electrically conductive) outer sheath and cast tungsten carbides as a filling. With respect to cast tungsten carbides (eutectic mixture of WC-W_2C), W_2C has the largest share with 73–80 wt %. The stoichiometric WC has a carbon content of 6.13 wt%, whereas W_2C has a lower carbon content of 3.61 wt% [18].

So far, the phase evolution of arc sprayed Fe-based WC-W_2C reinforced coating systems has not yet been examined. A few studies investigated the microstructure formation and phase transformation of arc sprayed Ni-based WC-W_2C reinforced coating systems [3,9]. According to these studies, eutectic tungsten carbides decarburized during spraying and a large amount of W dissolved into the Ni-rich matrix. Moreover, Ni also dissolved into WC-W_2C and gathered around WC-W_2C grains to form fine WC-W_2C–Ni composites. In [9] it was stated that these metallurgical interactions are attributed to the electrode phenomena during atomization, when the WC-W_2C grains are wetted by the molten metal. It was mentioned that these metallurgical interactions can lead to a degradation of the mechanical properties. The stoichiometric WC decomposes above 3058 K to L + C (L = liquid melt) in an inert gas atmosphere or vacuum, respectively [19]. Exposed to oxygen, the decomposition starts at significantly lower temperatures of approximately 823 K. With W_2C, congruent melting and the formation of liquid phases occur above a liquidus temperature of 3058 K. Two eutectic phases form during the cooling of the melt. A peritectic decomposition of W_2C to W + WC occurs at a temperature of 1523 K. Eta carbides (e.g. M_3W_3C, M_6W_6C etc.) are mainly formed according to Kurlov et al. [20] with heterogeneous microstructures, especially in the interface of WC and the transitional metal. The stoichiometries as well as the matrix material influence the phase stability [21,22].

Besides the chemical composition of the metal matrix, the degree of dissolution of the tungsten carbide depends on type, shape, and size of the carbides. For instance, irregularly shaped particles are more prone to dissolve due to their tendency to heat up to higher temperatures by the exposure of a heat source [23]. Small sized particles tend to dissolve faster than coarser particles. Moreover, as reported by other researchers [24,25] eutectic tungsten carbides are more susceptible to react with the liquid melt than more thermally stable carbides such as mono crystalline carbides consisting of hexagonal WC.

For tribologically stressed surfaces, it was found that the wear resistance of WC-composites depends, inter alia, on the embedment of hard phases [26,27]. Accordingly, the process control requires a good embedding and adhesion of hard particles in the layer composite, so that the contacting surface is not damaged due to breakouts of weakly embedded hard phases. In that respect, an insufficient adhesion of hard phases can lead to a damage of the surface integrity, the counter body or layer composite itself.

Regarding the manufacturing route of arc sprayed coatings using cored wires, there is no possibility to deposit coatings with graded carbide content. The local reinforcement due to hard particles is determined by the amount of hard particles used as a filling. Accordingly, the amount of hard particles cannot be varied via the running wire feed. The hard particle content can thus not be locally changed. The use of an external powder injection could be one approach to vary the amount of hard material in the coating to locally strengthen functional layer areas (Fig. 1). Accordingly, the potential of using functionally graded coatings in the field of toolmaking for the sheet metal forming industry (e.g. deep drawing tool) was already emphasize within the scope of the Collaborative Research Centre SFB 708 (DFG; German Research Foundation).

With regard to external hard particle injection in TWAS, initial approaches have already been described by Wilden et al. [28], who developed a modified arc spraying device in which powders are injected into the primary gas stream. Experiments using several material combinations demonstrated the possibility to embed single particles. However, an insufficient wetting of particles was observed. As a result, an adequate adhesion could not be established for the insertion of steel particles in a Zn-based and Al-based matrix. Furthermore, the investigation showed that the injection of particles into the axially incoming gas stream has a significant influence on the atomization of the molten electrode tips. Accordingly, the gas flow was disturbed, resulting in a more heterogeneous microstructure and topographical irregularities. Another approach of external powder injection is executed by means of an injection just behind the arc burning zone. Barbezat and Warnecke [29] have a patent on this approach. With the use of a modified arc spraying device and spray torch, a powdered additive material is fed axially into the arc burning zone via the primary gas stream or through the additional injector behind the arc burning zone. A closer examination of this modification or the generated layer systems cannot be found in the literature. Paczkowski et al. [30] analyzed the applicability of producing particle-reinforced layer systems by means of an open wire arc spraying system. Accordingly, different MMCs were produced using a Cu-based matrix. Metallographic investigations revealed a homogeneous distribution and a form-fitting embedding of the hard particle phase in the surrounding Cu-based matrix. Metallurgical interactions across the interface of hard particles and the metallic matrix were not investigated. Nevertheless, it was found that the particle loading of the atomizing gas stream stabilized the plasma at the arc burning zone. Dubovoj et al. [31] further examined the production of composite materials by means of external powder injection into the high-temperature region of the arc burning zone. Various metal-polymer, metal-ceramic, and metal-glass composites were investigated with respect to their mechanical and physical properties. According to this study, a major objective was the wear behavior, adhesion, and thermal conductivity of the coatings. Metallurgical investigations on the embedment of hard particles into the surrounding metallic matrix were not taken into account. In contrast to the aforementioned examinations, in this study the manufacturing route of an external injection of tungsten carbides and their embedding into the metallic matrix across the deposits are investigated. For this purpose, the embedment of tungsten carbides in coatings produced by conventional cored wires is compared with that manufactured with exclusively externally injected tungsten carbides. Therefore, the transition zones between the tungsten carbides and surrounded iron-based matrix are fundamentally investigated by means of scanning electron microscopy and nanoindentation. By using X-ray diffraction, the occurred phases can be traced back to the manufacturing process and the embedment of the tungsten carbides.

2. Experimental

2.1. Approach

In order to inject hard particles into the arc burning zone, a simple nozzle attachment was installed. Within this study, the Smart Arc 350 PPG arc spraying system (Fa. Oerlikon Metco, Switzerland) was utilized. A commercially available nozzle configuration with a cylindrical shape was used as an atomization nozzle inlet. The hard particles are radially injected into the arc burning zone next to the nozzle outlet. Fig. 2 visualizes the process of hard particle injection. The position and orientation of the injection needle can be adjusted depending on the injection parameters such as the powder feed rate and carrier gas flow. The experimental setup enables the required access and provides real-time recordings during the process by means of high-speed camera imaging, type Fastcam SA2 (Fa. Photron, Japan). Our objective is to ensure a sufficient wetting of injected hard particles at the molten wire tips, when the particles pass the realm of the molten pool of the steel wire tips. It has to be ensured that the radial powder injection needle does not become an obstacle within the axial gas flow. Moreover, since the structural components are mainly manufactured of electric