Journal of Alloys and Compounds 749 (2018) 10–22

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Laser synthesis and microstructure of micro- and nano-structured WC reinforced Co-based cladding layers on titanium alloy

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ARTICLE INFO

Article history:
Received 22 December 2017
Received in revised form
16 March 2018
Accepted 18 March 2018
Available online 21 March 2018

Keywords:
Laser cladding
Ti–6Al–4V
Preplaced powder
Microstructure
Interface
Wear

ABSTRACT

Micro- and nano-structured WC reinforced Co-based cladding layers on Ti–6Al–4V substrates were synthesized by laser cladding. The structure, phase composition, and wear behavior were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD), and friction-wear tests. High-angle annular dark field-energy dispersive spectroscopy (HAADF-EDS), transmission electron microscopy (TEM) and lattice images confirmed the XRD and SEM results. The interfaces exhibited good metallurgical bonding between the cladding layer and substrate owing to their high chemical affinity for each other. The cladding layer was composed of α(α′)-titanium, eutectics of $CoTi_2$, β-titanium, TiC, eutectics of TiC–TiB_2, VC (Cr_3C_2), (Ti, W)C_{1-x}, W, TiB_2, and Co_3W_3C phases formed by the dissolution of WC. VC inhibited grain growth more effectively than Cr_3C_2 or the combined effects of VC and Cr_3C_2. The wear resistance of the micro-/nano-WC cladding layers was markedly improved compared with those of Ti–6Al–4V. Nano-WC tended to convert into tungsten, however, the cladding layers easily became hard and brittle owing to aggregates of carbides or oxides. This effect resulted from interfacial boundaries formed by major differences at the α-Ti/α-Ti (Cr_3C_2, TiB_2) interfaces in terms of the chemical and structural contributions to the surface energy.

1. Introduction

Laser cladding is a surface modification process that uses a high-power laser beam to melt a deposited material onto a substrate to form a pore- and crack-free coating 50 μm–2 mm thick [1]. Comparing with the conventional coating, laser clad shows more advantages in terms of the integrity, the character of the interface between the cladding and the substrate, the degree of local surface modification, and the chemical composition control [2,3]. Hence, laser cladding is convenient for rapid manufacture of structures and component repair [4]. The ability to repair a component can save time with low cost compared with replacement by a new component [5].

Ti–6Al–4V alloy is widely used in the aerospace, marine, and chemical industries [6,7], as well as in biomedical devices and components [8]. Enhancement of the tribological properties of titanium alloy is of major interest for many applications [9,10] and various surface modification processes have been proposed to meet the different needs [8,11–13]. Among these, laser cladding is an effective method for manufacturing precise and defect free cladding layers of dissimilar materials to achieve surfaces with high wear resistance [11].

Laser cladding can be executed in different ways: through the use of a pre-placed powder [12], powder delivery [13], powder injection [1,14], and wire-based laser metal deposition [15]. In laser cladding, the powder plays a key role in the properties of the final coating [16,17]. Therefore, it is important to select the highest-quality powders. Fe– [18–21], Co– [12,22,23], and Ni-based alloys [24,25] have been used as binder materials. Research proposed by Näkki et al. [16] indicated that powders containing low amounts of impurity elements were most resistant to hot cracking. In addition to blends of powders, spherical WC particles can be injected directly onto the Ti–6Al–4V substrate without binder materials [26].

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https://doi.org/10.1016/j.jallcom.2018.03.235

Combinations of titanium substrates and cobalt-based claddings have been developed to obtain Co-based cladding layers on Ti–6-Al–4V substrates [12,27]. Cracking and delamination were the easily formed in the cladding systems [28]. Majumdar et al. [12] fabricated a Co–Ti clad layer with a compositionally graded interface on Ti–6Al–4V substrates. The increase in the hardness could be attributed to the presence of β-cobalt at the interface and of Ti-based intermetallic compounds [29,30]. Barekat et al. [31] investigated the oxidation behavior of the Co-based cladding layer. An amorphous nanocomposite cladding layer was also fabricated [32]. The addition of rare earth elements to metals has been shown to refine and purify the microstructure of cladding layers, by reducing porosities and cracking, leading to improved tribological properties of the cladding layers [33–36]. Moreover, rare earth elements also play an important role in the amorphization of cladding layers [37].

Tungsten carbide exhibits excellent wear resistance, making it an ideal material for cladding powders [38]. Amado et al. [39] reported that if an excessive power density was used, round WC particles dissolved into the substrate. This process causes nucleation and growth of WC crystals, which replace WC particles in the cladding core [38–41]. Generally micro-sized particles are used to improve the ultimate tensile and the yield strength, but with deteriorated ductility with high particle concentration [42]. Nanocrystalline WC–Co materials have been the subject of interests and focus of research programs owing to the expectations that the mechanical behavior of the material may improve significantly when grain sizes reduce to nanometer scale [43].

Nano-structured WC grain can improve the wettability and ductility and has been used to strength the materials, while maintaining good ductility, high temperature oxidation resistance and better corrosion resistance [44]. Nanoparticles (NPs) can be manufactured by several approaches, including hydrothermal, sol-gel technique, chemical co-precipitation, laser nano-manufacturing, reverse-micelle, the template synthesis, glass-crystallization, chemical vapor deposition, salt melt and spray pyrolysis method [45,46]. In addition to grain size, grain boundary stability provides an alternative dimension for producing novel nanograined metals with desired morphology and extraordinary properties [47]. The characterization of nano grain, interface and grain boundary is helpful to understand the synthesis mechanism and relation between the microstructure and properties [48–50].

The present research aims to investigate the influence of powder deposited on the cladding layers, discuss the WC dissolution, interface boundaries and the formation of η-carbides through exploring microstructure and wear resistance of micro- and nano-structured WC reinforced Co-based cladding layers on Ti–6Al–4V alloy and the characterization of interface in the multi-element system.

2. Experimental

An annealed 6-mm-thick Ti–6Al–4V titanium sheet was used as the substrate. The chemical composition (wt. %) was: 6.0 Al, 4.0 V, 0.15 O, 0.15 Fe, 0.004H, 0.02C, 0.01 N, and titanium (Bal.). As shown in Table 1, the deposited materials consist of tungsten carbide (WC) and Co-based alloys (ST-NANO, Co., Ltd. China). The sizes of micro-WC and nano-WC are 1 μm and 80 nm respectively. The Co-based alloys conclude: Co (1 μm), Si (0.5 μm), B (0.5 μm), Cr_3C_2 (50 nm), VC (50 nm), ZrC (30 nm), and Y_2O_3 (50 nm). The chemical compositions of the Co-based alloy are shown in Table 2. Each mixture was milled to ensure a uniform dispersion of the powders. All the powders were blended for 3 h at 300 rpm in argon atmosphere at room temperature. Where, alumina ball (Al_2O_3) was selected as the milling media and the ball to powder size ratio was 20:1. After ball-milling and drying, the powder was mixed with 5 wt % acetyl cellulose and diacetone alcohol for use as the laser cladding precursor.

Laser cladding was performed by placing the powder blends on a Ti–6Al–4V substrate, and melting the powder using a 5-kW maximum output YLS-5000 fiber laser (IPG, USA) with a KR60-HA robot (Kuka, Germany) and BIMO QBH laser processing head (HIGHYAG, Germany). Argon was used as a shielding gas at a flow rate of 15 L min^{-1} to protect the cladding from oxidation. The laser beam, with a wavelength of 1075 ± 5 nm, was focused on the surface of the target materials. The laser spot size was 5 mm. The parameters for the laser cladding was: power, 1.4 kW; scanning speed, 5 mm/s; defocus, 20 cm.

After the laser cladding process, the cladding was etched with Murakami's reagent [10 g $K_3Fe(CN)_6$], 10 g NaOH, and 100 mL H_2O and dilute aqua regia containing 2 mL HF, 10 mL HNO_3, and 88 mL H_2O.

The microstructure of the cladding layer was characterized by X-ray diffraction (XRD), a field emission scanning electron microscope (SEM), and field transmission electron microscope (TEM). The XRD measurements were performed on an X'Pert PRO X-ray diffractometer (PANalytical B. V., Netherlands) with Cu Kα radiation (λ = 0.15406 nm). Scans were performed from 15° to 120° with a step size of 0.02626°. The scanning speed was 0.4376°/s at a beam current and voltage of 40 mA and 40 kV, respectively.

An S4800 SEM (Hitachi, Japan) equipped with an energy-dispersive spectrometer was used for microstructure observations and compositional analysis. The STEM samples were prepared using a FEI Helios 450 S focused ion beam system, (FIB; FEI, USA). STEM imaging was performed on a FEI Titan Themis 200 STEM (FEI, USA) with a CEOS probe aberration corrector operated at 200 keV.

The friction and wear properties of the cladding were measured with a HT-600 high-temperature tribometer. The sliding speed was 0.058 m s^{-1} and the sliding time was 60 min at a load of 1.14 kg under dry wear conditions. Ceramic Al_2O_3 balls with a diameter of 3 mm were selected as the counterpart. The wear mass loss of the samples was measured by an electronic balance with a minimal precision of 0.1 mg.

Table 1
Chemical compositions of powders used for laser cladding (wt. %); compositions of Co-1–Co-3 are shown in Table 2.

Specimens	WC	Co-based alloy
N1	25	75, Co-1
N2	25	75, Co-2
N3	25	75, Co-3
M1	25	75, Co-1
M2	25	75, Co-2
M3	25	75, Co-3

3. Results

3.1. Microstructure and phase constituents of the cladding layers

Fig. 1 shows the microstructure of a typical nano-WC cladding layer (N1) on a substrate. The cross-sectional view clearly shows overlapping regions among the first, second, and third layer with

Table 2
Chemical compositions of Co-based alloys (wt. %).

Co-based alloy	Cr_3C_2	VC	Si	B	ZrC	Y_2O_3	Co
Co-1	5	10	4	3.5	2	1.5	Bal.
Co-2	15	0	4	3.5	2	1.5	Bal.
Co-3	0	15	4	3.5	2	1.5	Bal.