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Laser gas assisted nitriding and characterization of tungsten surface

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ABSTRACT

Laser gas assisted nitriding of tungsten surface is carried out while incorporating the high pressure nitrogen assisting gas. Metallurgical and morphological changes in the laser treated layer are examined using the analytical tools. The nitride compounds formed in the surface vicinity are analyzed incorporating X-ray diffractogram and Fourier-transform infrared spectroscopy. The wetting state and the free energy of the laser treated surface is determined using the droplet contact angle method. The friction coefficient of the resulting surface is measured via microtribometer and UV visible absorption characteristic of the surface is analyzed. It is found that the laser texturing of tungsten surface results in micro/nano size pillars without forming micro-cracks and large size cavities. The laser treatment gives rise to hydrophobic surface characteristic with improved UV visible spectrum absorption coefficient. The microhardness increased significantly because of the nitride compounds formed at the surface and friction coefficient shows wave-like behavior because of the surface texture.

1. Introduction

Tungsten nitrides retain superior physical and chemical properties and they find wide applications in various industries including electrocatalyst for hydrogen generation [1], electrochemical storage materials [2], and etc. They possess high electronic and thermal conductivities and show ceramic material behavior such as high hardness coefficient [3]. Tungsten nitrides are the possible candidates for coating material towards improving wear and oxidation-resistant of tool parts. In general, tungsten nitrides are difficult to prepare because of the challenges of incorporation of nitrogen into the tungsten lattice, which is thermodynamically unfavorable at atmospheric ambient pressure [4]. Different processes were developed using high pressure and temperature synthesis methods [5,6]. Some of these processes involve with multi-steps and high costs. One of the alternative techniques is to introduce high power laser processing under the high pressure assisting gas ambient. However, laser heating process is associated with high temperature and high cooling rates, and the thermal stresses generated in the heated region remains critical for surface defects such as cracks and voids. The laser treatment with crack free processing can be possible through introducing regularly distributed and closely spaced laser scanning tracks on the surface. The heat conduction among the regularly distributed scanning tracks alters the cooling rates while creating the self-annealing effects in the surface vicinity of the treated layer [7]. This arrangement provides crack free surfaces with the treatment layer thickness in the order of tens of micrometers [8]. In laser processing, an assisting gas undergoes reactions with the superheated molten material in the irradiated region. This gives rise to various oxide or nitride compounds formation in the treated region depending on the nature of the assisting gas employed [9]. However, the depth of diffusion of these gases is shallow because of the laser short heating duration. Nevertheless, the surface characteristics in terms of hardness and scratch resistance [10], and electrochemical response [11] change significantly after the laser treatment process. Some of the compounds formed in the treated surface, such as nitrides, can be fruitful for various applications in sensing and photoactive devices, which is particularly true for tungsten substrates [12]. Consequently, investigation of laser surface treatment of tungsten under high pressure nitrogen assisting gas and characterization of the resulting surfaces become essential.

Considerable research studies were carried out to examine laser surface treatment of metals and alloys under nitrogen assisting gas ambient. Laser treatment of composites including tungsten was presented previously [13,14]. The findings revealed that compound layer was formed at the treated surface, which comprised of α-Ti, WC, W_2C, TiC, W and (W, Ti) $C1_x$ phases. The W_2C and TiC phases were formed and distributed in titanium matrix with different

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shape at different locations of laser treated layer [13]. In addition, WC particles were distributed throughout the treated layer as enforcement phase, which occurring metallic bonding with matrix. The presence of WC and TiC phases in the metal matric composite layer enhanced the microhardness and abrasion resistance of the surface [13]. However, monitoring of the integrity of the process towards securing the the process accuracy remained important [14]. In this case, the probe beam reflection (PBR) and laser plume emission spectroscopy (PES) could be incorporated for the online monitoring system, which facilitated a simultaneous prediction of surface characteristics [14]. Tungsten particle mixing of alloy surfaces via laser processing [15] and synthesis of tungsten nitride coating by a laser beam ablation became important for high temperature surface treatment applications [16]. The melt pool size of the laser treated surface became laser pulse intensity dependent; hence, the maximum temperature and flow velocity in the melt pool could vary with the pulse intensity distribution [15]. Moreover, as nitrogen pressure was increased during the laser processing, the stoichiometry of the nitride compounds and hardness improved significantly [16]. The selective laser melting and treatment of tungsten and tungsten alloys was studied by Ivekovic et al. [17] and He et al. [18]. Because of the intrinsic properties of the treated surface, the laser selective melting of tungsten was involved with challenging tasks, mainly involved with cracked and/or porous parts; however, the proper selection of the laser treatment parameters minimized these adverse effects [17]. In addition, laser treatment involving with control surface texturing resulted in superhydrophobic surfaces with a maximum water droplet contact angle of 162° and a minimum rolling angle of 1.0° after fluoroalkylsilane modification on the textured surface [18]. Although the laser gas assisted treatment of tungsten carbide tiles was challenging in terms of surface asperities such as microcracks and large size voids, via controlling the laser treatment parameters asperity free surfaces could be resulted [19]. Because of the metallurgical changes in the laser treated layer such as formation of lamellar and acicular morphology composing of WC–W_2C dense layer, the microhardness increased at the surface significantly [19]. However, the fracture toughness of the treated surface reduced considerably due to microhardness enhancement at the treated surface and the residual stress in the surface vicinity became compressive [19]. Ultra-nano- and nano-crystalline tungsten-based coatings via pulsed laser deposition technique was important for improved mass density and stiffness of the coating [20]. The vacuum annealing of laser deposited amorphous like coatings resulted in the nucleation of ultra-nano crystalline seeds, which was embedded in an amorphous matrix and the stiffness improvement was related to the interplay between the crystal size and the density [20]. The assessment of tungsten carbide wettability in laser cladded metal matrix composite coating was important and the molten pool lifetime greater than 0.68 s exhibited proper wetting of tungsten carbide particles with the surrounding matrix [21]. However, at high cooling rates, the delaminating of ceramic particles from the metal matrix under the tensile load took place, alternatively, under the slow cooling rates, the particles stayed intact with the metal matrix while improving the wear properties of the coating. However, too slow cooling rates resulted in settlement of tungsten carbide particles at the bottom of molten pool reducing the wear resistance of the coating [21]. The fabrication of various shaped tungsten micro-pin arrays using micro-carving process was studied by Park et al. [22]. They demonstrated that high percentage of tungsten was detected on the core micro-pin structure; however, relatively large percentage of oxygen was found on the recast layer (O 9%, W 91% in the center area, and O 53%, W 47% in the outer area). Investigation of additive manufacturing of tungsten carbide-cobalt substrate via selective laser melting processes was carried out by Uhlmann et al. [23]. They focused on the behavior of the agglomerated and pre-sintered tungsten carbide-cobalt (WC-Co) powders in the selective laser melting processes. The findings revealed that, depending on the exposure parameters, various types of micro structures could be generated and the original material profile could be changed significantly during the laser material interactions. The nitridation of one-dimensional tungsten oxide nanostructures was examined by Varga et al. [24]. They showed that, simultaneously, bandgap energies significantly decreased in the calcination process and the photo-activity in the treated samples was not improved by the decrease of the bandgap. This behavior might be explained with the deterioration of charge carrier transport properties of the materials due to the increased number of structural defects (acting as trap states). The laser ablation of thin tungsten layers deposited on a carbon substrate was investigated by Paris et al. [25]. They indicated that it was possible to estimate tungsten coating thickness, but it was not detectable spectroscopically for a complex coating process when the tungsten layer was covered with a diamond-like carbon.

Although laser heating and texturing of tungsten and its compounds were studied previously [19], the main focus was to investigate the effects of the tungsten hard particles (WC) on the laser treated layer characteristics such as the microhardness and the scratch resistance. The influence of the high pressure nitrogen assisting gas on the microstructure and the mechanical properties of tungsten was left for future study. Consequently, in the present study, laser surface treatment of tungsten at high pressure nitrogen assisting gas environment is carried out and the resulting surface characteristics including texture parameter, wetting state, microhardness, friction coefficient, and absorption of UV visible spectrum are examined. Analytical tools including scanning electron microscope (SEM), atomic force microscope (AFM), energy dispersive spectroscopy (EDS), X-ray diffractogram, Fourier-transform infrared spectroscopy (FTIR), and UV visible spectrometry are incorporated. The micro-tribometer is used to assess the friction coefficient of the laser textured surface while goniometer is incorporated to assess the wettability of the resulting surface.

2. Experimental

Tungsten workpieces of 3 mm thickness were used in the laser treatment experiments. The CO_2 laser (LC-ALPHAIII) was used to scan the tungsten surfaces with a constant scanning velocity. The nominal laser output power was 2 kW and the irradiated spot diameter was in the order of 200 μm at the workpiece surface. High frequency repetitive pulses (1500 Hz) were incorporated during the constant speed scanning at the surface. The overlapping ratio for the irradiated spots at the surface, due to high frequency repetition, was in the order of 70%, which in turn formed the regular laser scanning tracks on the treated surface. Nitrogen with 99% purity at high pressure (600 kPa) was used as an assisting gas during the laser treatment of the workpiece surfaces. In order to avoid several repeats towards securing the defect free surfaces in the experiments, the initial tests were carried out to select the laser treatment parameters. The selected laser parameters resulted in treated surfaces with free from asperities, such as micro-cracks, voids, and large size cavities. The findings after the initial tests showed that reducing the laser power by 10% while keeping the laser scanning speed same resulted in small size texture height without forming the micro/nano pillars at the surface. Alternatively, reducing the laser scanning speed by 10% while keeping the laser output power same as pervious, cracks and cavities at the surface were resulted. Therefore, incorporating the proper settings of laser parameters; such as power level, beam intensity distribution, pulse repetition rate, spot size, and the scanning speed,