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Mechanical properties of DLC coating sputter deposited on surface nanocrystallized 304 stainless steel

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ABSTRACT

Surface nanocrystallization (SNC) can markedly improve surface mechanical properties of metallic materials and accelerate thermal diffusion of elemental atoms. In this work SNC is used as a pretreatment method to improve mechanical properties of the DLC coating on the 304 stainless steel. Surface mechanical attrition treatment (SMAT) was used to generate a nanocrystalline surface layer on the steel substrate. Then the DLC coating with Cr adhesive interlayer was sputter deposited on the coarse-grained and the surface nanocrystallized steel substrates (noted as CG-DLC, SNC-DLC samples, respectively). X-ray diffraction confirms an amorphous nature of the carbon coating. Elemental analysis by energy dispersive X-ray reveals the enhancement of Cr diffusion into the steel substrate for the SNC-DLC sample. The microhardness, scratch, Rockwell-C indentation, cyclic impact and wear tests show that the SNC-DLC sample has higher surface hardness and load-bearing capacity than the CG-DLC sample. The mechanical tests also evidence that the SNC-DLC sample possesses higher film cohesion strength and better wear resistance as compared to the CG-DLC sample. Mechanisms for the enhancement of cohesion and adhesion strength of the DLC coating on SNC stainless steel substrate are discussed. This work may provide an advantageous hybrid processing for improving surface mechanical properties of austenitic stainless steel and other relatively soft structural steels compared with the conventional duplex treatment consisting of thermal–chemical processes (nitriding, carburizing, etc.) and hard coatings.

1. Introduction

Surface engineering plays an important role in modern machinery industry. Hard coatings have elongated service life of tools and molds; however, there is problem for application of hard coatings in machine parts that are made of soft steels such as stainless steels, low alloy steels and so on [1]. Hard coatings with small thickness have low load-bearing capacity, and plastic deformation of the soft substrates may lead to premature failure of the coatings under high-applied loads [2].

A measure to reduce the so-called 'eggshell effect' is to apply thermal–chemical processes such as nitriding, carburizing, oxidizing, etc. for the metallic substrates before deposition of hard coatings [3–8]. By this pretreatment, the obtained surface diffusion layers with thickness up to several hundreds of micrometers may provide enough support for hard coatings. However, nitrogen atoms at the top surface of the nitride layer will be redistributed during coating deposition for several mechanisms, and even 'black layer' at the interface can be formed, which deteriorates coating adhesion [9]. Processing parameters of the duplex treatment have to be precisely controlled in order to avoid adverse effects of the nitride layer.

In the recent decade, surface nanocrystallization (SNC) has drawn intensive research interests in material science and surface engineering [10]. Through surface mechanical attrition/grinding treatment (SMAT/SMGT [10–13]), ultrasonic shot peening or other mechanical methods, nanocrystalline surface layer can be generated on pure iron, low-carbon steels, stainless steels and other metallic materials. This nanocrystalline surface layer has higher hardness and toughness than the coarse-grained substrate, and is featured with graded grain size at the depth direction, thick plastic deformation layer (up to 200–300 μm), and high adhesion to the substrate. Surface mechanical properties of the treated metallic substrates are thus markedly improved by single SNC treatment or SNC combined with thermal diffusion processes of nitriding [12,14], chromizing [15], aluminizing and so on.

Austenitic stainless steels are widely used in industrial, biomedical and other applications mainly due to their excellent corrosion

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resistance; however, the low hardness and poor wear properties impose strong limitations in many cases [16]. Diamond-like carbon (DLC) coating that has better corrosion resistance, higher hardness and wear resistance is thus used to surface modify austenitic stainless and other steels [17,18]. Nevertheless, its adhesion to steel substrates is limited due to the large difference in physical properties (i.e. hardness) of the materials [19]. Enhancement of the steel substrates and modification of the DLC coating are carried out to deal with this problem. For the steel substrates, plasma nitriding or carburizing can effectively improve hardness, wear resistance and fatigue properties of austenitic stainless steels through the formation of the interstitial supersaturated, hard and metastable S-phase [2,4–6,16]. For the DLC coating, gradient or multi-layered film structures and doping the film with Si, Cr, Ti, etc. are used to improve adhesion and other mechanical properties of the DLC coating on the thermal-chemically pretreated austenitic stainless steels and other metallic substrates [1,3,5,8,19].

Surface nanocrystallization of austenite stainless steels of 304, 316L, 321, etc. has been well studied [14,20–22]. Surface nanocrystallization can markedly increase surface hardness of the 304 stainless steel, and improve mechanical properties of the subsequently deposited CrN film [23] and TiN film [24]. In this work, surface nanocrystallization by SMAT is used as a pretreatment to enhance the 304 stainless steel substrate for the sputter deposited DLC coating. Interface structure, hardness, adhesion, impact behavior and tribological properties of the DLC coating on the coarse-grained and the surface nanocrystallized stainless steel substrates are comparatively studied.

2. Experimental

2.1. Sample preparation

AISI 304 stainless steel plates with the size of $20\times20\times5$ mm^3 were ground with SiC papers down to grits 1200, polished with 10 μm diamond paste, and ultrasonically cleaned in deionized water, acetone and then ethanol for use (noted as coarse-grained, or CG samples). The grain size of CG samples was in the range of 30–50 μm. The CG samples were subjected to SNC treatment at an ultrasonic SMAT machine using Φ2 mm stainless steel balls. The treatment was stopped for 1–2 min after every 3 min treatment. The total treatment time was 15 min. Flowing air was also used to cool down the sample during the treatment. The samples were then polished with care to remove the contaminated surface layer, and ultrasonically cleaned (SNC samples).

The DLC coating was deposited onto CG and SNC stainless steel substrates with a closed-field unbalanced magnetron sputtering system (UDP650, Teer Coatings Ltd., UK) comprising six rectangular cathodes [25]. Two pure Cr targets and four pure graphite targets were used in the deposition system. The equipment was furnished with a substrate holder rotated at a speed of 5 rpm. The substrate was biased with pulse DC at a frequency of 250 kHz. The chamber was evacuated to a background pressure of 4×10^{-4} Pa prior to deposition, and then the steel substrates were sputter cleaned at a bias of −450 V for 30 min in order to remove the surface oxide layers and contaminants. The flow rate of Ar gas was set at 30 sccm, resulting in a working gas pressure of 0.17 Pa.

In the deposition stage, a thin adhesive Cr layer of about 0.2 μm thickness was prepared at first, then a composition gradient layer of CrC_x (~0.4 μm) was made for load support, and finally the pure carbon top layer (~1.4 μm) was deposited by only sputtering graphite targets with a power of ~2 kW. The gradual variation of chemical composition in the transition layers was beneficial for the improvement of adhesion strength to the substrate. The bias voltage was remained at −80 V, and the deposition rate of pure carbon films was ~0.7 μm/h. All the depositions were carried out without additional heating or cooling of the substrates. The coating samples with coarse-grained and surface nanocrystallized substrates were noted as CG-DLC and SNC-DLC samples, respectively.

2.2. Characterization and mechanical tests

Morphology and elemental composition of the samples were analyzed with a scanning electron microscope (SEM, FEI Quanta 600FEG) equipped with energy dispersive X-ray analysis (EDX, INCA, Penta FETx3), and crystallography was examined by X-ray diffraction (XRD, CuK_α, Rigaku D/MAX-2400). Microstructure of the samples was characterized with a transmission electron microscope (TEM, JEM 2010) operated at 200 kV. Cross-sectional TEM foils were prepared and ion-thinned at low temperature.

Hardness of the samples was measured at the surface and the cross-section with a microhardness tester (TuKon 2100B). Scratch test and Rockwell-C indentation test were used to evaluate coating adhesion of the samples. The scratch test was carried out at a home-made scratch tester, in which the diamond indenter had a tip curvature radius of 200 μm. During test, the load was set as constant (10 N, 20 N, 30 N, 40 N), and the lateral moving speed of the indenter was 3.0 mm/s. For the indentation tester, the tip curvature radius of the indenter (TCY-A) was 200 μm, and the loading rate was 2.2 N/s (9.2×10^{-4}–2.8×10^{-1} mm/min). Cyclic impact test was done by a tester described in [26], with a Φ5 mm WC ball as the punch. The impact rate was 10 Hz, the impact load was 400 N, and the impact distance was 0.75 mm. The pin-on-disk wear test was conducted at a tribometer (CETR UMT-2), with the counter body of a Φ10 mm GCr15 ball. The linear speed was set as 10.5 cm/s during test.

3. Results

3.1. XRD analysis

X-ray diffraction shows that austenite (γ) and a little martensite (α′) phases are detected for CG sample (Fig. 1a). Strain induced martensite may be generated within the surface layer of the 304 stainless steel by mechanical polishing, and the biphasic layer can be removed by chemical polishing [27]. The SMAT process further increases the content of martensite at the surface layer of the SNC sample [14,21]. For the DLC coating samples, the main peaks are from the substrates (Fig. 1b), confirming the amorphous nature of the DLC film. The peaks at $2\theta=44.3°$ and $2\theta=64.3°$ can be attributed to α′ martensite as well as Cr (ICDD #6-694), which is from the Cr interlayer. For SNC and SNC-DLC samples, the latter has smaller intensity ratio of α′(110)/γ(111). This reveals the thermal-induced inverse γ/α′ phase transformation, which occurs at above 573 K [21].

3.2. Cross-sectional optical, SEM, TEM and EDX analyses

Optical and SEM micrographs of the etched cross-sections of CG and SNC samples are shown in Fig. 2. In the optical micrograph, the SNC sample has a dark surface layer with the thickness around 300 μm, which would reveal the deformation layer by SMAT. At the higher magnification by SEM, abundant shear bands are seen at the depth larger than 60 μm from the surface. The shear bands intersect at an angle of about 70° or parallelly cut through the whole grains, as reported in [28].

The microstructure of the SNC sample is further analyzed by TEM. The grain size is about 20 nm at the surface (Fig. 3a), much smaller than that of the CG sample (30–50 μm). The continuous diffraction rings in the insert indicate random orientation of the grains. The grain size appears to be around 100 nm at the depth of 30 μm, and the discontinuous diffraction rings with spots are from diffracting of a few grains (Fig. 3b). The grains become even larger at the depth of 60 μm, and many nano-twins are observed at the depth of 120 μm (Fig. 3c,d). The gradient microstructure and the grain refinement process of the