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Novel chemical process for preparing h-BN solid lubricant coatings on titanium-based substrates for high temperature tribological applications

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ABSTRACT

Hexagonal boron nitride (h-BN) coatings prepared from a polyborazylene (PBN) polymeric precursor were deposited on titanium-based substrates and annealed via infra-red irradiation in a rapid thermal annealing (RTA) furnace. Crystallized h-BN coatings were obtained by adding Li_3N as a catalyst at a relatively low annealing synthesized temperature (~1200 °C). The resulting coatings had a thickness of 15 μm and were evenly coated and homogenous. The coating/substrate adhesion was evaluated by the micro-scratch test, with the value of best critical load occurring at approximately 12 N against a Rockwell C diamond point. This adhesion increased with the growth of the additive ratio of Li_3N. The friction coefficient measurements were carried-out by tribological testing at 360 °C using a cylinder/disk configuration. Stainless steel 15-5PH cylinders were used as counter bodies to the titanium disk. The friction coefficient was reduced from 0.72 for the Ti/stainless tribosystem to 0.35 for the Ti/h-BN/stainless tribosystem.

1. Introduction

The reliability of aeronautic and aerospace tools, such as titanium-based alloys, is limited by the lifetime of certain critical mechanical components exposed to severe conditions, including elevated temperature (>350 °C), corrosive and oxidizing atmosphere and wear. Within this context, development of protective coatings on these metallic pieces rubbing in a dry friction tribosystem is absolutely necessary. Furthermore, these protective coating materials should be considered as a non-risk for the environment according to the recent REACH (Registration, Evaluation, Authorization and Restriction of Chemical substances) regulation adopted by Europe in 2007.

Two general categories of coating can be applied [1]. The first category enhances the hardness of the metallic substrate by deposition of a hard coating, such as Cr^{III}-based, cobalt-based, nickel-based, c-BN and inorganic (DLC) coatings [2,3]. The second category includes soft coatings, such as graphite, molybdenum disulfide and PTFE, which are used to decrease the shear stress of the micro-junctions that can be easily deformed [4]. Among these soft materials, h-BN is considered one of the most promising materials for protecting metal components in engineering. As well as being known for its good lubricating properties, h-BN also exhibits other desirable properties, such as high thermal conductivity, low electrical conductivity and excellent thermal stability [5–7].

The h-BN coatings used in this study were prepared by the polymer derive ceramics (PDCs) method described previously [8]. In comparison to traditional sputtering [9], PLD [10], atomic layer deposition [11] or CVD [12], the PDC method presents a variety of advantages, including a deposition process with tailored thicknesses on substrates belonging to all classes of materials, even for the substrates with complex forms. The use of PBN as polymeric precursor is dominant due to the ease and reproducibility of its synthesis. Moreover, given this B/N ratio close to 1, this polymer is ideal candidate to produce stoichiometric h-BN, and there are no contaminants except hydrogen atoms, which can be easily removed during the ceramization step [13–15].

Annealing processes at high temperatures (>1200 °C) are necessary for the polymer-to-ceramic conversion. However, this temperature is unsuitable for metallic substrates due to their low melting temperatures. Recently, much effort has been made to replace the conventional thermal treatment needed for ceramic conversion with a rapid thermal annealing (RTA) through infrared (IR) irradiation to keep the metal's integrity [8]. The mechanism of this annealing process is briefly described by the metallic substrate reflecting IR radiation and causing only the pre-ceramic coating to absorb heat during irradiation by thermal conduction. This prevents the metal from melting and has been shown to produce promising coatings on titanium substrates under these conditions. However, the reported coating displays a rather low h-BN crystallization ratio, which can be optimized to ensure the best

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lubricating behavior of h-BN. In previous work, we pointed out the effect of lithium nitride (Li_3N) as a crystallization promoter to produce highly crystallized h-BN at a temperature of only 1000 °C. The lowering of the onset crystallization temperature may expand the possible h-BN coating on metallic substrates [16].

In this paper, we present the structural characterization of h-BN coating prepared from PBN with and without the aditivation of Li_3N. The adhesion of the h-BN/ titanium alloy was measured by micro-scratch testing. The tribological properties of the as-deposited coating on the Ti6242 alloy against stainless steel were investigated by cylinder-on-disk line-contact reciprocating-sliding at 360 °C under the specific conditions (temperature, pressure) representative of the aeronautical industry.

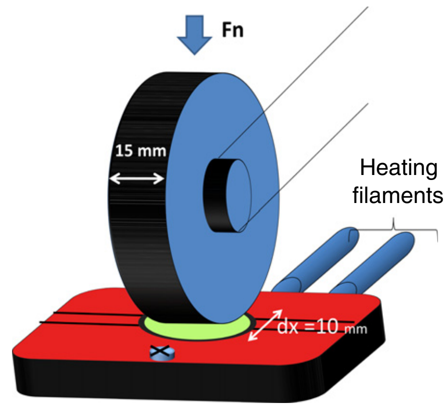

Fig. 1. The configuration of cylinder-on-disk line-contact reciprocating-sliding on a Cameron-Plint tribometer.

2. Experimental procedure

2.1. Coating preparation

Pure PBN ($(B_3N_3H_4)_n$) was synthesized via a polymerization reaction from a borazine ($B_3N_3H_6$) monomer according to a previously published procedure [17]. Li_3N was used as a promoter, and microsized Li_3N powders in 1, 3 or 5 wt.% were added to PBN to produce LiBN01, LiBN03 and LiBN05 samples, respectively. The mixture was stirred for 30 min in a schlenk tube under argon.

Metal substrates were successively washed by ethanol and distilled water and coated with pure PBN or the mixture of PBN and Li_3N by dip-coating the Ti–6Al–2Sn–4Zr–2Mo–0.1Si (composition given in mass%, referred as Ti-6242) substrate. All coatings were prepared in a glove box filled with argon. Coated samples were kept at 200 °C for 1 h to induce stabilization of the raw coating by an advanced polymer reticulation. Samples were placed in a RTA cold wall chamber furnace (AS-One, ANNEALSYS) and heated to 1200 °C following an annealing process described previously by our group [8].

2.2. Characterization equipment

Structural characterization was carried out by X-ray diffraction (XRD) analysis (Phillips PW 1830/40) with a CuK radiation source at room temperature. Micro-scratch tests were performed in increasing load mode (ILM) on commercial equipment (MST-CSEMEX-CSM) equipped with a Rockwell tip (radius, $R = 0.2$ mm), integrated optical microscope, acoustic emission (AE) detector and a tangential force sensor (Ft) with a detection sensitivity of the order of 10 mN [18]. The Cameron Plint (TE77) high frequency friction machine is a very versatile reciprocating tribometer doped with a heating filament to heat the contact surface up to 360 °C. It was used to characterize the wear and friction behavior of the stainless steel cylinder/h-BN coating/ Ti-6242 tribosystem, and the configuration is shown in Fig. 1, with Δx; the movement distance of the sample ($\Delta x = 2.5$ mm), F; the frequency of the test (F = 5 Hz), and H_a; the average contact pressure ($H_a = 100$ MPa). The cylindrical counter body used in this study was stainless steel 15-5PH.

3. Results

3.1. Morphology and structural characterization

Fig. 2 shows typical SEM images of the different h-BN coating samples, LiBN0, LiBN01, LiBN03 and LiBN05, prepared under the same conditions described previously. Following an annealing process under the RTA furnace at 1200 °C, the transparent raw polymer became a white ceramic coating. The surface of the sample LiBN0 (Fig. 2a) appears uniformly dense and homogenous, with full coverage on the substrate surface and no remarkable defects. The presence of Li_3N involves some defects on the coating surface (Fig. 2b, c and d). The formation of these defects is due to the removal of H_2 produced by the polymer degradation and boron nitride crystallization reactions. Besides, at high temperature Li-based species could evaporate leading to more defect. Thus, the defect density was visibly increased with the quantity of Li_3N added in the coating (see Fig. 2b, c and d).

Despite the presence of defects at the coating surface, the morphology was not the most important parameter in the quality of lubricant coating, contrary to the hard protective coating. The mechanism of the lubricant process involves easy delivering and deformation of the coating materials under shear stress. Nevertheless, in some industrial cases, the morphology is a critical parameter for setup processing. In this context, the sample with more than 5 wt.% of Li_3N would not be considered, as the morphology of these coatings was unacceptable.

The thermal and chemical stability and lubricant properties of h-BN are closely associated with its crystalline degree. XRD was performed on all of the samples, and the results are shown in Fig. 3. Many signals were observed in all 4 patterns, and part of them can be attributed to titanium contained in the Ti-6242 alloy (JCPDS file 089-3073) and/or the interphase compounds (TiN, JCPDS file 087-0633 and TiB_2, JCPDS file 089-3923). Our previous work demonstrated that during the annealing process via infrared irradiation, reactions occur between BN and Ti at the interface, leading to a new interphase composed of TiN and TiB_2 that is several microns thick [8]. This interphase enhanced the coating/substrate adhesion thus increasing the sample life-time. H-BN crystallinity is generally characterized by peaks at 26.7° for (002) and 41.8° and 43.2° for (10) crystallographic planes [19]. Peaks at 42° to 45° could not be clearly distinguished from those of the substrate and interphase for samples deposited on Ti-6242 alloy. Therefore it is reasonable to focus our analysis on the signal at $2\theta \approx 26.7°$. The XRD pattern recorded on LiBN0 sample presents a broadened peak shifted at $2\theta = 25.1°$, meaning that the average crystalline area is small, according to the Scherrer's equation (see Table 1). Moreover, the lattice parameter, d, can be obtained using the Bragg's law. The calculated value, $d = 0.36$ nm, is more important than the h-BN's theoretical one (0.33 nm) revealing a disorder arrangement. Moreover, we can see that the full width at half maximum, $FWHM$, of this peak becomes narrower and shifted toward the theoretical position of crystallographic planes at 26.7° with the increase of the Li_3N ratio in the initial mixture. This variation means that under the same thermal treatment process, Li_3N with an h-BN coating becomes remarkably more crystallized. In addition, the degree of crystallinity increased with the promoter ratio in the pre-mixture. Table 1 records the measurement values for the (002) diffraction plane position, its $FWHM$, the interlayer lattice, d_{002}, and the calculated values for crystalline dimension, L_{002}, obtained by using Scherrer's equation [20].

To evaluate the microstructure of the coating, HRTEM was carried out on sample LiBN05. A representative HRTEM micrograph, shown in Fig. 4, shows the hexagonal phase of BN. SAXD reveals bright