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Hybrid gas phase Ti-B-C-N coatings doped with Al

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ABSTRACT

Deposition of Multicomponent hard coatings (Ti-B-C-N) on the molybdenum high-speed tool steels (AISI M52) has been achieved by mixed vapor deposition technique to improve the mechanical properties of the surface. The Ti-B-C-N coating samples were produced by a hybrid gas phase process, were in this technique, the coating materials that supplied in the gas phase were produced from powders that vaporized by thermal energy (that is, PVD- Reactive Evaporation Process), while the reactor that used to deposit Ti-Base coatings is a hot-wall chemical vapor deposition (HWCVD) system equipment. The resulting coating exhibit different amounts of the Titanium oxide phase, which is characterized by the low mechanical and thermal properties. These phases (Ti-O) will have determinant effect on the coated high speed steel tools. The alloying of transition metal nitrides and borides (TiN, BN, and TiB) with stable oxide-forming elements (for example, Cr, Al, Si and Ni) will have the effect of decreasing crystallinity, promoting nanocrystalline structure and increasing oxidation resistance. Ti-Base hard film was characterized by XRD technique, and Scanning Electron Microscopy (SEM). Mechanical characterization of the hard films has been performed by using The Ball-on-disk wear tests. With different deposition temperatures (550–950 °C) and at the same reactive gas flow rate 2.5SLPM (Standard Litter Per Minute), Al doping in the Ti-B-C-N coating has proven a great success by producing a new film microstructure (free of Ti-O phases) which contains fine fiber structure as a strengthening second phase in the Ti-B type structure with a sufficient amorphous phase (B-N) as a matrix. Maximum hardness of 4230 HV is achieved, with better thermal stability during the process of the wear test than the uncoated H.S.S samples. Also a great enhancement in the wear resistance values for this coating film (Volume loss = $1.8291*10^{-7}$ mm^3) was reported.

1. Introduction

High-speed tool steels are the toughest materials; however, their relatively low wear resistance limits their application to low-speed machining (Cutting speed may be defined as the relative speed between the cutting tool and the surface of the work piece) [1,2]. There is, however, a tradeoff between wear resistance and toughness that can limit the application of these super hard tools to lighter Cutting speed. For the production of nanostructured or composite coatings, it may be necessary to combine two or more of the deposition methods that were mentioned earlier in one system. These coatings certainly represent a new class within the very broad field of surface engineering and are the result of breakthrough developments in physical and chemical vapor deposition (PVD and CVD) technologies in recent years [3]. Titanium base coatings had been used in the coating of tool steels since the mid-sixties to increase tool life, improve the surface quality of the product, and to increase the production rate. In this work different metal powders were used to synthesize the Ti-B-C-N coating by reactive evaporation with the use of a reactive gas (NH_3) at 2.5 SLPM flow rate at different deposition temperatures (550–950 °C) in the hot-wall chemical vapor deposition (HWCVD) system equipment. In Reactive evaporation, the difficulties involved in direct evaporation processes due to fragmentation of the vaporized compounds are overcome in reactive evaporation, where a metal is evaporated in the presence of the reactive gas. In reactive evaporation, a partial pressure of reactive gas is used to deposit compounds of the vaporized material by the reaction of deposited

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atoms with ambient gases [4–7]. The CVD process can be defined as the deposition of a solid on a heated surface via a chemical reaction from the vapor or gas phase [6]. This combination (CVD and PVD) that shown in Fig. 1, will result in technical and financial advantages that are; 1- The use of pure metal powders will produce a coating film that is free of chlorine content which is a major element in the Ti, B, and Al gases (chlorine will cause the tool hardness to be decrease after few months) [1]. 2- The use of metal powders greatly reduces the cost of using very expensive gases such as $TiCl_3$, $TiCl_4$, BCl_3, and $AlCl_3$. 3- Also this technique has proven great futures to overcome the main limitations that associated with gas phase deposition process such as pulsed leaser deposition or other PVD and CVD process [7–10]. This advantages can include the not restricted to a line-of-sight deposition which is a general characteristic of sputtering, evaporation and other PVD processes, also the above mentioned gases are consider to be extremely toxic (this is not the case of our precursor) and must be neutralized, which may be a costly operation [2,10]. Finally this technique will result in a high deposition rate and thick coatings that can be readily obtained due to its flexibility that it allows many changes in composition during deposition [8–11].

2. Experimental method

Multicomponent hard coatings (Ti-B-C-N) were deposited on a molybdenum high-speed tool steels (AISI M52) containing 0.9% C (Table 1). The Ti-B-C-N coatings doped with Aluminum was deposited at different deposition temperatures (from 550 to 950 °C), and under the same nitrogen flow rates (2.5SLPM). A mixed gas phase deposition process technique (PVD and CVD) in Fig. 1 were used in this work as a new rote for the hard film deposition. This system mainly consists of four units as follows: 1- The Powder evaporation unit used in this work consist of high temperature vacuum tube furnace type GSL-1600-60X that used to supply the metal gases for the deposition process. 2- Gas delivery system, is used to supply all needed gases into the chambers in a controlled manner, (it's consists of three feeding lines namely: Ti-Base vapor, N_2 gas and NH_3 gas). 3- Deposition Chamber, is the reactor to deposit Ti-Base coatings, it is a two stage furnace, that was constructed from 304 L Stainless Steel material as a pipe with 700 mm in length and 2" in diameter with Alumina tube, which represented the deposition region and its contain inside a glass tube (1/2 in dia.) that made from quartz for the purpose of obtaining clean surface film. 4- The exhaust gas system to release all the non-reacted chemical substances and by products of the reaction. Different metal powders, a pure Titanium powder with purity of 98.5% that provided by Fluka (Switzerland) with average particle size of 9.989 μm, Titanium carbide powder (TiC) provided by High Media (India) with average particle size of 1.263 μm, and Boron powder with purity of 98.5% provided by Merck (Germany) with average particle size of 32 μm. In all experiments the starting powder weight was in the percentage of was 35%Ti, 50%B, 5%TiC, and 10% for Al powder.

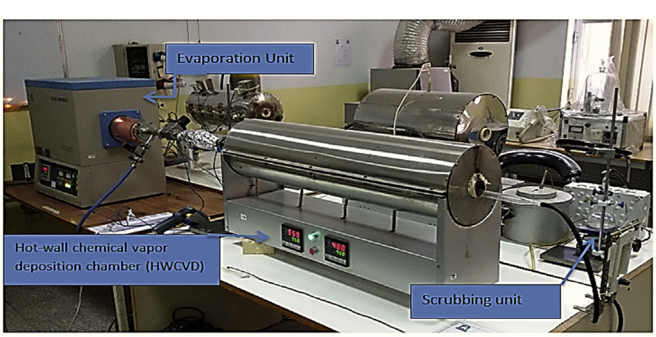

Fig. 1. Mixed gas phase deposition process system equipment.

The gas phase was produced from powders that vaporized by thermal energy (that is, PVD- Reactive Evaporation Process), while the deposition route was based on the CVD deposition technique. The produced Ti-Base hard film was characterized by X-ray diffractometer (XRD-6000 Shimadzu x-ray diffractometer with incident angle of 0.154 nm using Cu-Kα radiation) to investigate the phase constituents. The average grain size for the produced phases in the Ti-B-C-N hard film was measured by applying the Scherer empirical formula that is based on the XRD parameters and its resulting pattern. The topographical features of the top surface for Ti-B-C-N coatings at different deposition conditions was carried out by using Tescan VEGA 3SB scanning electron microscope with Accelerating Voltage: 200 V to 30 kV and the magnification power from 6× to 100,000X. All samples were coated with a thin layer of Gold by sputtering system to make the samples conductive at least at the surface to prevent the accumulation of electrostatic charge at the surface. Also Vickers micro Hardness tester– South Korea device was used to test the hard metal substrate (High Speed Steel sample) hardness before and after deposition of the Ti-based coating layer. This was made by using major load of 0.98 N that is controlled by a regulator. The pin-on-disk wear tests were carried out by using a Microtribometer testing machine-USA under lubricant-free sliding conditions, the testing was performed at room temperature (22 ± 2 °C) and a relative humidity of 50–70%. The normal load applied on the sample surface was 10 N, which was controlled by a load suspension system. The test counterpart was a 6 mm diameter of martensitic steel ball (AISI 52 100), which was sliding in a circular path with a radius of 3 mm at a velocity of 250 rpm.

3. Results and discussion

3.1. XRD results

Figs. 2–6 show the XRD patterns for Ti-B-C-N coatings doped with Aluminum that was deposited at different deposition temperatures (from 550 to 950 °C), and under the same nitrogen flow rates (2.5SLPM). The choice of precursors and deposition temperature influences chemical composition, crystallite, micro hardness and wear properties of the coating. No homogenous deposition film can be detected under 600 °C (for the deposition temperature) as can be seen in Fig. 2 for the Ti-B-C-N coatings doped with Al that was deposited at 550 °C, only iron and aluminum oxide with the chemical formula of α-Al_2O_3, that contains 52.93 Al wt.% and 47.07 O_2 wt.% of Rhombohederal structure with a very low peak intensities. In Fig. 3 the increase in the deposition temperature results in a change in the presented phases, the presence of iron (ferrite with a cubic structure of 100% Fe), and titanium oxide mixed with iron that contain 36.81 Fe wt.%, 31.63 O_2 wt.% and 31.56 Ti wt.% (Rhombohederal structure) can be detected in this pattern. Also aluminum oxide and boron nitride with a chemical formula of (BN) and cubic structure which contains 43.56% B and 56.44% N can be detected in this Figure. It has been reported by many researchers that the deposition rate rises with higher deposition temperatures [12,13]. At higher deposition temperatures the XRD peaks for α-Al_2O_3 phases in Fig. 4 that was deposited at 750 °C exhibit an increase in peak intensity, in addition to peak broadening. By applying the Scherer empirical formula, the resulting phase average grain size indicating a grain growth for Al_2O_3 phase that was estimated to be ~9 nm with T_d = 600 °C, to abut ~14 nm with T_d = 750 °C. One important notice that has been reported by other