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Abstract. In recent times, friction and wear in relation to the deposited carbon films on the steel substrates are important issues for industrial applications. In this research study, solid thin films were deposited on the stainless steel 304 (SS 304) substrates under different operating conditions. In the experiments, natural gas (97.14% methane) was used as a precursor gas in a hot filament thermal chemical vapor deposition (CVD) reactor. Deposition rates on SS 304 substrates were investigated under gas flow rates 0.5 – 3.0 l/min, pressure 20 – 50 torr, gap between activation heater and substrate 3.0 – 6.0 mm and deposition duration 30 – 120 minutes. The obtained results show that there are significant effects of these parameters on the deposition rates on SS 304 within the observed range. Friction coefficient of SS 304 sliding against SS 314 was also investigated under normal loads 5 – 10 N and sliding velocities 0.5 – 1.0 m/s before and after deposition. The experimental results reveal that in general, frictional values are lower after deposition than that of before deposition.

1. Introduction

Chemical vapor deposition (CVD) is a technique by which chemical precursors are transformed into the vapor phase to decompose on a heated substrate to form a thin solid film. The formation of films can be epitaxial, polycrystalline or amorphous based on the material and reactor characteristics. In recent years, CVD can be considered as a promising process of film deposition in semiconductor industry due to its high throughput, high purity, and low cost of operation. CVD is extensively used in optoelectronics applications, optical coatings, and coatings of wear resistant parts. The deposition rate which is the major concerned parameter in a CVD process is significantly dependent on the generation of required species to be deposited and its transportation into the vapor and surface kinetics [1]. There are several parameters which affect the deposition rate significantly such as temperature of the substrate and filament, gas flow rate, gas composition, chamber pressure etc. on different types of materials [2-4]. Experimental results as well as numerical models of thermal conduction and diffusion have clarified that the mass transport in the gas phase indicates a considerable role at the time of thin film growth, and this thin film growth is mostly controlled by the mass transport rate rather than by the surface reaction rate at substrate temperature. Celii et al. [5] noted that variation of the gas flow rate could affect remarkably the resultant microcrystalline diamond (MCD) crystal texture and surface morphology but has less effect on the growth rate. It has been reported that thin film growth by hot

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filament CVD are related with a mass transfer controlled process and the growth rate was increased by increasing the gas flow rate, while other groups of researchers have suggested that the gas flow rate does not play a significant role on thin film growth. The effects of gas flow rate and the gap between activation heater and substrate on the deposition rate on SS 314, SS 202 and carbon steel were investigated [6-8].

In the present research, an effort has been made to investigate the deposition rates on stainless steel 304 substrates under different operating conditions using thermal CVD technique. With its remarkable physical properties, thin film coatings on different substrates are expected to have many applications in industrial and engineering fields. Low friction coefficient and low wear rate are two desirable properties which make it suitable for machining. During friction test, friction coefficients of deposited and non-deposited stainless steel materials in relation to normal load and sliding velocity were investigated. It is expected that the application of these results will contribute to the improvement of different concerned mechanical processes.

2. Experimental details

2.1 Chemical and Mechanical Properties of Tested Materials and Experimental Conditions
The chemical and mechanical properties of SS 304 are listed in Tables 1 and 2. The experimental conditions for CVD and tribology tests are shown in Tables 3 and 4.

Table 1: Chemical composition of SS 304

Elements	C	Si	Mn	P	S	Cr	Ni	Fe
Min. (Wt%)	0.08	1.00	2.00	0.045	0.025	18	8.0	Balance
Max. (Wt%)	1.2	1.00	2.02	0.047	0.030	20	10.5	Balance

Table 2: Mechanical properties of SS 304

Density	Hardness (Brinell)	Hardness (Rockwell B)	Tensile Strength, Ultimate	Tensile Strength, Yield	Modulus of Elasticity	Poisson's Ratio	Shear Modulus
8 gm/cc	170	75B	505 MPa	215MPa	193-200 GPa	0.29	86 GPa

Table 3: Experimental Conditions (For CVD)

Sl. No.	Parameters	Range/conditions
1.	Substrate	SS 304
2.	Reactant gas	Natural gas mostly Methane (CH_4)
3.	Substrate size	20mm×20mm
4.	Surface roughness	0.25 μm
5.	Distance between activation heater and substrate	3.0-6.0 mm
6.	Flow rate (CH_4 gas)	0.5-3.0 l/min
7.	Pressure	20-50 torr
8.	Substrate heater temperature	825-850°C
9.	Activation heater temperature	1250-1450°C
10.	Deposition duration	30-120 mins

Table 4: Experimental Conditions (Tribology tests)

Sl. No.	Parameters	Operating Conditions
1.	Normal Load	5-10 N
2.	Sliding Velocity	0.5-1.0 m/s
3.	Relative Humidity	65 ($\pm$ 5)%
4.	Duration of Rubbing	30 minutes
5.	Surface Condition	Dry
6.	Disc material	Deposited and non-deposited: SS 304
7.	Pin material	SS 314
8.	Surface Roughness of SS 314, R_a	0.65 μm

2.2 CVD Unit and Tribometer for Tribological Test
To deposit diamond like carbon, a thermal chemical vapor deposition unit was used. Frictional tests were carried out using a pin-on-disc tribometer.

3. Results and discussion

3.1. Experimental Results for Deposition Rate under Different Operating Conditions
In this study, deposition rates on SS 304 are investigated at different operating conditions. The deposition rates can be measured in two ways: (i) the deposition rates of the coating in gram per unit time (g/min) can be calculated from the weight difference of SS 304 substrate before and after deposition and (ii) the deposition rates of the coating in microns per unit time (μm/min) can be calculated from the thickness difference of SS 304 substrate before and after deposition. In this research, deposition rates were calculated from thickness difference of SS 304 before and after deposition.

3.1.1 Effect of Gas Flow Rate on Deposition
To observe the effects of gas flow rate on deposition rate of SS 304, several experiments are conducted for the substrate surface roughness 0.25 μm, substrate heater temperature 825-850 $^{\circ}$C, activation heater temperature 1250-1450 $^{\circ}$C, distance between activation heater and substrate 3.0 mm, deposition duration 60 mins and pressure 25 torr. These results are presented in figure 1. Results show that deposition rate on SS 304 increases for the gas flow rate from 0.5 l/min to 2.0 l/min. That is, within this range, lower values of deposition rate are observed at flow rate 0.5 l/min and then the values of deposition rate increase almost linearly at a maximum value up to flow rate 2 l/min. For the flow rate higher than 2 l/min, the deposition rate decreases and it is very low at 3 l/min. The cause behind this fact is the rate of reaction is more at lower gas flow rate due to more period of sustainability of methane gas in to reactor chamber than that of higher gas flow rate.

The process of CVD thin film growth can be divided into two steps: (i) the transport of active species and (ii) the incorporation of carbon atoms into the substrate lattice. Under fixed conditions of activating source gases, the production rate of active species is fixed and the thin film growth depends on the rate of these two steps, that is the transport rate of source gases to the substrate surface and the rate of thin film growth reactions on the growth surface. The surface growth process is controlled by a mass transport process rather than the reaction rate occurring in the growth surface [5]. The direction of gas flow does not influence the thin film growth rate of substrate and growth is affected by the mass diffusion. If the gas flow rate near the growth region is sufficiently strong, convective mass transport will play an important role in thin film growth and gas flow rate markedly affect the growth rate of thin film [5]. The complex chemical and physical processes, which occur during CVD, comprise several different but interrelated features. The process gases of the chamber before diffusing toward

the substrate surface pass through an activation region (a hot filament), which provides energy to the gaseous species. This activation causes molecules to fragment into reactive radicals and atoms, creates ions and electrons, and heats the gas up to temperatures approaching a few thousand Kelvin. Beyond the activation region, these reactive fragments continue to mix and undergo a complex set of chemical reactions until they strike the substrate surface. At this point the species are adsorbed and entrapped within the surface, some portions are desorbed again back into the gas phase, or diffuse around close to the surface until an appropriate reaction site is found. If a surface reaction occurs and the conditions are suitable, then the thin film coating deposits on the substrate. During this process, the higher the gas flow rate, the higher the density of carbon particles is obtained. That is more the density of carbon particle, more amount of deposition on the substrate may be occurred. The increase of deposition rate might be due to elimination or reduction of the local energy barrier during the chemical activity by increasing the gas flow rate. One of the conditions required for high deposition rate is that the diffusion of gas toward the substrate is the rate-determining stage and the high flow rate made this mechanism possible. At high flow rate, diffusion and convection are equally important. The flux of carbon-containing species on thin film growth surface is higher at higher flow rate. Celii et al. [5] suggested that the changes of carbon-containing species flux with gas flow rates were responsible for the changes in the morphology of the deposited thin films. These results are in partially agreement with the results for up to a certain range of gas flow rate [6,7].
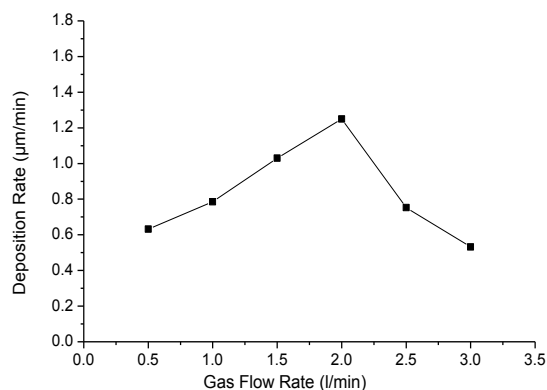

Figure 1. Variation of Deposition Rate (µm/min) with the Variation of Gas Flow Rate for SS 304

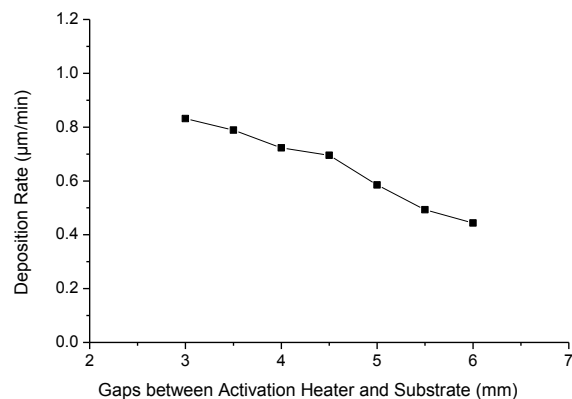**Figure 2.** Variation of Deposition Rate (µm/min) with the Variation of Gaps between Activation Heater and Substrate for SS 304

3.1.2 Effect of Gap between Activation Heater and Substrate
The experimental conditions such as, gas flow rate 1.0 l/min, surface roughness 0.25 µm, substrate heater temperature 825-850 ^{o}C, activation heater temperature 1250-1450°C, duration 60 min, pressure: 25 torr are maintained to understand the effect of gap between activation heater and substrate on deposition rate on SS 304 substrate. Within these conditions, the gaps between activation heater and substrate: 3.0, 3.5, 4.0, 4.5, 5.0, 5.5 and 6.0 mm are selected. The obtained results in figure 2 show that deposition rate decreases with the increase in gap between activation heater and substrate. The number of activated carbon species and atomic hydrogen are more near the activation heater [1]. As the gap between activation heater and substrate reduces, more amounts of activated carbon species may be deposited on substrate and hence increase the deposition rate (coating thickness and weight of deposited materials). The trends of these results are almost similar to the results of other research works related to thin film deposition on different substrate materials [7,8].

3.1.3 Effect of Pressure

To analyze the influence of vacuum pressure on deposition rate, different pressures within the reactor chamber 20, 25, 30, 35, 40, 45 and 50 torr were considered. The deposition rate on tested SS 304 is increased with the increase in pressure. These experimental observations are shown in figure 3. During experiment, the operating conditions such as, surface roughness 0.25μm, gas flow rate 1.0 l/min, distance between activation heater and substrate 3.0 mm, substrate heater temperature 825-850 ^{o}C, activation heater temperature 1250-1450 ^{o}C and duration 60 mins are maintained. In fact evaporation is a common method of thin film deposition. The source material is evaporated in a vacuum. The vacuum allows vapor particles to travel directly to the target object (substrate), where they condense back to a solid state. It is apparent that, in general, as the vacuum level increases, more carbon species deposit on SS304 but at higher pressure, the deposition rate is much higher.

3.1.4 Effect of Duration

Variation of deposition rate with the variation of deposition duration is shown in figure 4. Different durations such as 30, 60, 90 and 120 minutes are considered to study the deposition rate. In the experiments, gas flow rate 1.0 l/min, surface roughness 0.25 μm, distance between activation heater and substrate 3.0 mm, substrate heater temperature 825-850 ^{o}C, activation heater temperature: 1250-1450 ^{o}C and pressure 25 torr were considered. It can be seen that deposition rate increases almost linearly with the increase in deposition duration. It is certain that, for a particular set of operating conditions, deposition rate is a function of deposition duration.
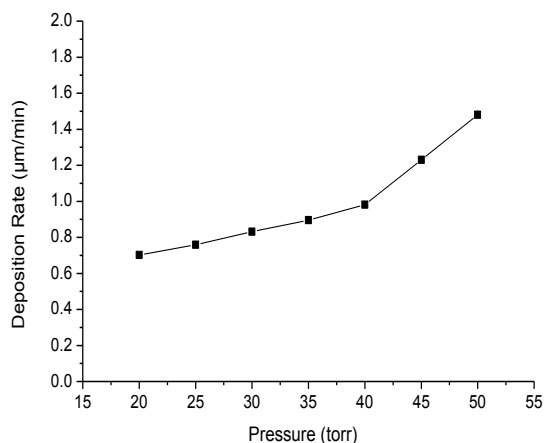

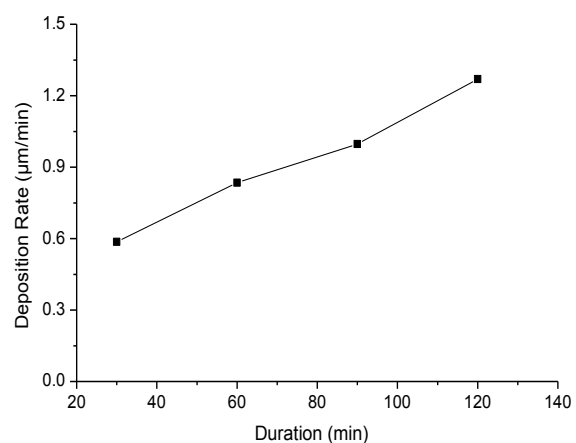**Figure 3.** Variation of Deposition Rate (μm/min) with the Variation of Pressure for SS 304

Figure 4. Variation of Deposition Rate (μm/min) with the Variation of Duration for SS 304

3.2 Frictional Properties of Deposited and Non-deposited Substrates

Figure 5 shows the variation of friction coefficient with the variation of duration of rubbing for deposited and non-deposited substrates. Experiments were carried out at normal load 7.5 N, sliding velocity 0.75 m/sec, relative humidity 65%. The dotted and solid curves indicate the friction coefficients before and after deposition, respectively. These curves show that at early stage of rubbing, friction coefficient is low and then increases almost linearly up to certain value and after that it remains constant for the rest of the experimental time. At starting of experiment the friction force is low due to contact between superficial layer of pin and disc. Then the friction coefficient increases due to ploughing effect and because of roughening of the disc surface. After a certain duration of rubbing, the increase of surface roughness and other parameters may reach to a certain steady value and for this

reason the values of friction coefficient remain constant for the rest of the time. It is apparent that the steady values of friction coefficient are lower for after deposition than that of before deposition. After deposition, lower values of friction coefficient are obtained under deposition conditions than that of before deposition conditions for the normal loads ranging from 5 to 10 N and sliding velocities ranging from 0.5 to 1.0 m/s. The obtained results are shown in figures 6 and 7.
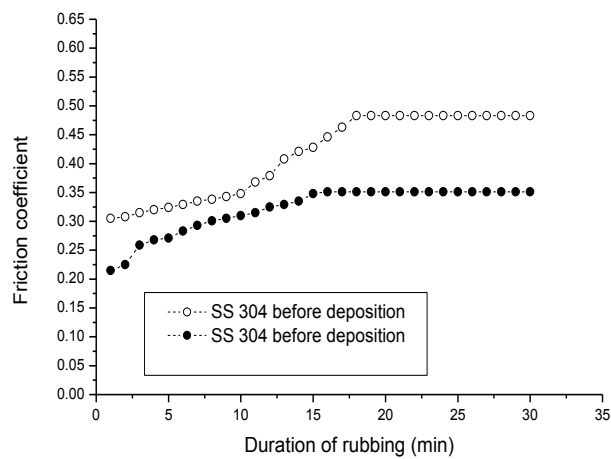
Figure 5. Variation of Friction Coefficient with the Variation of Duration of Rubbing before and after Deposition
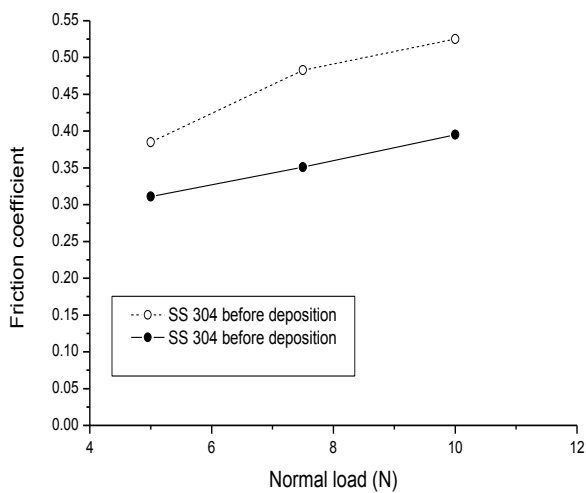
Figure 6. Variation of Friction Coefficient with the Variation of Normal Load before and after Deposition
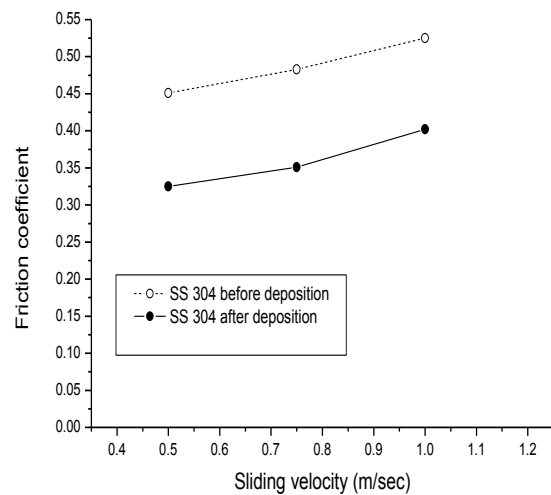
Figure 7. Variation of Friction Coefficient with the Variation of Sliding Velocity before and after Deposition

3.3 FESEM and Microscopy Analysis

3.3.1 Surface morphology analysis using FESEM
Surface morphology of deposited and non-deposited SS 304 substrate was examined by using JEOL JSM 7600F Field Emission Scanning Electron Microscope (FESEM). The obtained results are

presented in figure 8. Microstructural examination revealed that carbon species were mainly incorporated into the existing iron lattice as interstitial atoms or as a finely dispersed alloy precipitate in the diffusion layer. It is observed that the agglomerated carbide precipitates formed on the substrate surface. It is also noted that morphology of tested steel substrate indicates a semi granular uniform nanostructure formation under the test conditions. Finally it can be concluded that the carbon layer was dense and embedded somewhat uniformly into the substrate material. The surface restructuring revealed by FESEM analysis which leads to nanostructure formation is an apparently complex phenomenon resulting from the interplay and compromise between different competing and concurrent factors. The environmental conditions, i.e. high temperature and reducing atmosphere, will probably active surface reconstruction process- a result of oxide reduction and associated with nitrogen adsoption, leading to atomic and nanoscale chemical and structural rearrangement at the surface. Surface energy driven processes will nonetheless overlap with thermally activated processes, such as phase separation and transformation – in particular, carbide precipitation – and recrystallization, which in turn are particularly sensitive to the thermo-mechanical properties of the substrate material.
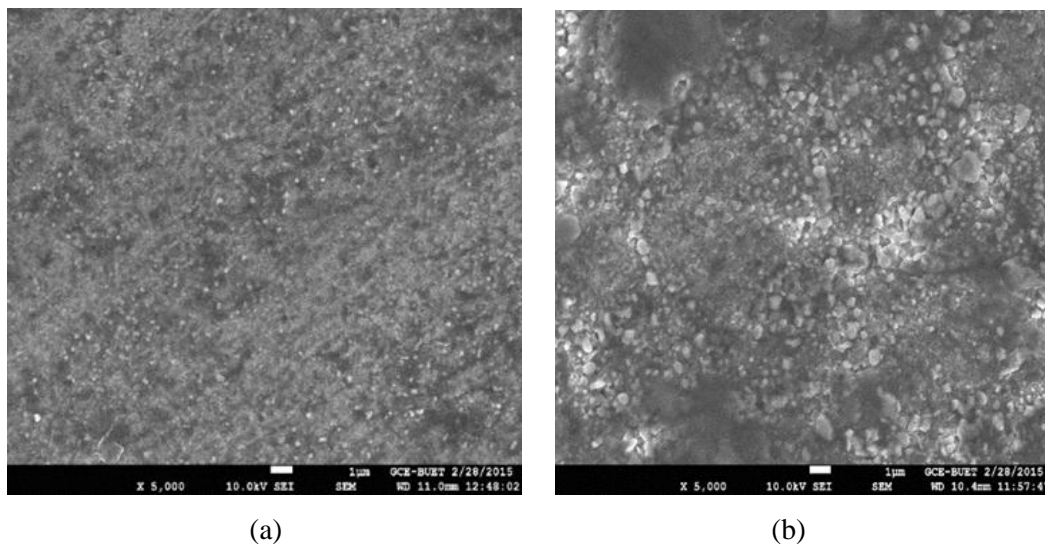

(a)   (b)

Figure 8. FESEM surface morphology of the deposited SS 304 at gas flow rate
(a) 0.5 l/min and (b) 2.0 l/min, magnification x 5000

3.3.2 Analysis of worn surfaces
Figure 9 shows optical micrographs of the worn surfaces for deposited SS 304 after friction tests. The appearance of the worn surface of SS 304 is clearly rougher at gas flow rate 0.5 l/min as compared with the flow rate 2.0 l/min. That is, the wear track of SS 304 is less rough and free from adhered material at gas flow rate 2.0 l/min. From these microscopic observations, it is apparent that for the optimum level of deposition rate, the lower the friction coefficient and hence less rough of the wear track after friction test.
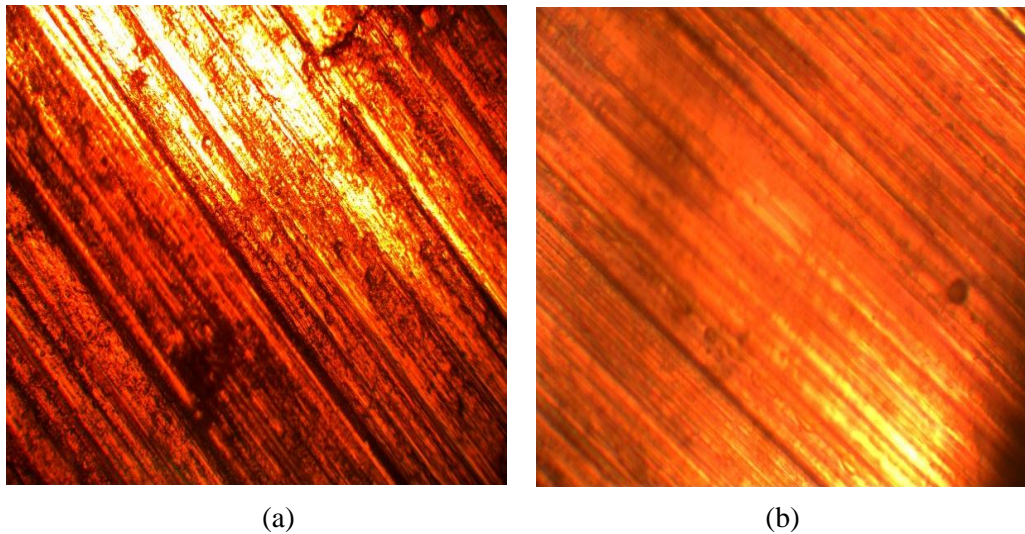
(a)   (b)

Figure 9. Optical microscopy of wear track after friction test of deposited SS 304 at (a) gas flow rate 0.5 l/min and (b) gas flow rate 2.0 l/min (100μm)

4. Conclusions

Gas flow rate certainly affects the deposition rate on SS 304 substrate. The deposition rate on SS 304 shows higher level of value at certain gas flow rates. Less or more than the certain gas flow rates, deposition rate is low. The major findings of this research study are to identify as well as specify the desired level of gas flow rate for obtaining highest possible deposition rate. It is concluded that deposition rate is a function of distance between activation heater and substrate, chamber pressure and deposition duration. The tribological properties are better in deposited conditions as compared to non-deposited conditions. The morphological analysis provides the evidence of real deposition process under certain conditions. The obtained results can be used as a valuable source for designing mechanical and tribological systems in order to improve the performance and quality in industry.

5. References

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