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Abstract

The present investigation is on the tribological behaviour of graphene coated bearing steel (EN31). Though bearing steel has excellent mechanical properties but its wear properties are inadequate. To enhance its wear properties, bearing steel was coated by graphene. Graphene is a very unique and peculiar material. It has excellent mechanical, chemical, electrical, magnetic and optical properties. Furthermore, it is light in weight which makes it one of the most sought after materials in the research world. To improve the adhesion property between graphene and bearing steel, bearing steel was first coated with nickel using electroplating technique. Then graphene was coated by CVD technique. To analyse the characteristics of graphene, Raman spectroscopy was carried out. The friction and wear tests were performed at constant load of 1 N and different speeds of 0.05 m/s, 0.075 m/s and 0.1 m/s for the tribological analysis of the materials. After wear, the worn out surfaces were further investigated by using scanning electron microscope (SEM). From the present investigation it has been observed that coated bearing steel shows improved tribological characteristics.

Keywords: Tribology, wear, friction, graphene, bearing steel

1. Introduction

Bearing steel is widely used to manufacture micro and small parts of machines and equipment like bearing components (ball, roller), ball screw, micro linear motion rail, pin gauge, etc. These components are subjected to sliding wear during their functionality. Though bearing steel has excellent mechanical properties, it has very moderate wear characteristics. In order to improve reliability in the performance, wear characteristics need to be enhanced. A lot of research has been done in tribology field to get an optimum result. The present investigation is about analysing the tribological property by utilizing the unique property of interesting material “graphene”. Here, in this study graphene is used as coating material. Several methods have been used to synthesize graphene coating. Some of them are mechanical cleavage, mechanical exfoliation, unzipping carbon nano-tubes, chemical vapour deposition and chemical reduction [1]. For fabrication of graphene layer, any of these techniques can be used according to quality, expense and adaptability. Properties and characteristics of graphene depend upon techniques employed for synthesis. One technique may be producing near perfect quality graphene, but if it is expensive, it cannot be used for industrial application. If expense is little, but quality is cheap, it also cannot be used. So, there should be a trade-off between these two. Some fabrication techniques will be helpful for mass production while some will be effective in high performance production for research purpose. Praveen Kumar and M F Wani suggests that scotch tape technique provides better quality of graphene but this process is costly. In terms of scalability, thin graphite method performs better but quality of graphene produced is very poor [2]. Among all these techniques, for inexpensive and large

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size graphene growth, CVD technique is one of the best approach. CVD has shown upper hand in growing graphene as it leads to produce a good quality coating with high yielding. Though there are some chances that graphene grown may wrinkle because of lack of similarity in coefficient of thermal expansion between substrate and graphene [3].

There are several materials which have the ability to dissolve carbon. This may result in formation of either carbide or graphene. To generate graphene layers, material should be selected in such a way that it should not form carbide. Instead it should end up in forming graphene layers. Mostly, transition materials like platinum, cobalt, nickel, copper, etc. are used for synthesizing graphene. These transition materials act as the catalyser. During heating of metal, precursor diffuses into the catalyst, then it reaches to a maximum limit. After that during cooling, carbon atoms segregate and help in forming graphene. Platinum is a very good choice as the catalyser. But high cost of platinum limits its usage as the catalyser. Among all the transition materials, nickel and copper are widely used for formation of graphene because of its low cost and easy availability. Because of poor solubility of carbon in copper, graphene formed is generally of single layer. But when nickel is used as the transition material, it has relatively better solubility of carbon than copper. Because of better solubility, precipitation of extra carbon atom occurs. This causes multi layered graphene formation. When graphene is grown by precipitation method, it requires a lot of attention in managing temperature, heating rate and cooling rate [4, 5]. Nickel is chosen for the role of catalyst in this paper. Nickel can be coated by different methods like physical vapour deposition, electro-less deposition, electroplating, etc. Selection of process depends upon several factors like uniformity, crystallinity, growth rate, cost, etc. From economic point of view electroplating is chosen for nickel coating on the bearing steel sample.

In synthesizing graphene, different precursors can be employed. The precursor can be in solid, liquid or in gaseous state. Like, acetylene in gaseous state, sucrose in solid state and hexane in liquid state has been used as the precursor. Generally the type of precursor is chosen depending upon quality, uniformity, number of layers to be synthesized, availability, cost and purity. Usually gaseous hydrocarbons are chosen as the precursor. Because of purity, easy availability and low cost, they are preferred over other types of precursors [6]. The reactant, in chemical vapour deposition technique, helps to catalyse the reaction. The reactant must be chosen in such a way that it should not diffuse into the transition material. The reactant also acts as the carrier. In this paper hydrogen is taken as the reactant. Hydrogen has low diffusivity in nickel. So its recombination and desorption occurs very quickly. So nickel remains open for absorbing hydrocarbon. This helps in quick diffusion of carbon atoms in the nickel surface [7].

Several studies have been performed to analyse the tribological performance of graphene. Bayram Yildiz et al. synthesised graphene on copper foil. Then they transferred it to the journal bearing. They found out wider worn out track on the non-coated journal bearing than the graphene coated journal bearing [8]. Philip Egberts et al. synthesised graphene on copper foil and found out that graphene lowers the friction and the bilayer graphene provided lower friction than the monolayer. They observed that there exists a very weak bonding between coating and substrate [9]. M Reguzzoni et al. coated graphene on various substrates and found out that monolayer graphene showed better anti-frictional characteristics than the multilayer graphene. He suggested that if the multilayer graphene can be bound to the substrate tightly its performance can be improved [10]. These studies clearly reveal the anti-friction characteristics of graphene. Several studies on graphene coating have been done on different substrate. To the best of our knowledge graphene coating has not been performed on bearing steel which finds a lot of applications specially in the bearing material.

In the present investigation, graphene is grown by low pressure chemical vapour deposition technique. Low pressure was employed to avoid any undesirable reactions and increase the chances of growing a uniform film. Here, acetylene (C_2H_2) is used as the hydrocarbon precursor. H_2 is taken as the carrier which also acts as a catalyser. By keeping nickel as the transition material, multilayer graphene was synthesized. Then graphene coating on nickel plated bearing steel specimen was characterized. Then by performing tribology test, wear characteristics of graphene coated bearing steel was investigated.

2. Experimental Procedure

2.1 *Material and sample preparation*

A bearing steel rod of 80 cm length and 26 mm diameter was procured from which specimens of 25 mm diameter and 8 mm thickness were made. Samples were made flat by using belt polishing machine of grade 80. Then samples were polished by using emery papers of grade 120, 220, 400, 600, 800, 1200, 1500 and 2500 in increasing order on grinding and polishing machine respectively (METCO, Chennai make). Polishing time on one grade of emery paper was approximately 20 minutes or up to a time in which marks generated by previous grade paper were eliminated. Then these samples were polished on clothes to get a burr and scratch free surface. During cloth polishing, diamond paste of grain size 5 µm was used as the abrasive and aerosol was used as the lubricant. Cloth polishing was carried out for approximately 5 minutes. Then samples were cleaned in digital ultrasonic cleaner (frequency 40 ± 3 kHz) by using acetone ($(CH_3)_2CO$), followed by ethanol (C_2H_5OH) for about 10 minutes to remove dirt particles and lubricant. Then the samples were dried and kept wrapped in butter paper so that they do not become contaminated. Now the samples were ready for the electroplating.

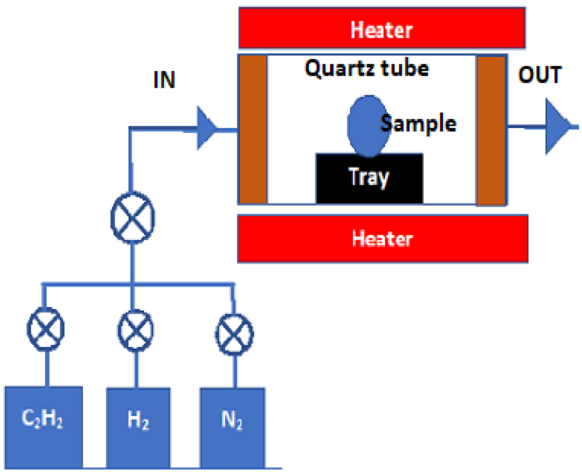

Figure 1. Schematic diagram of CVD setup

2.2 *Synthesis of graphene*

In electroplating, bearing steel sample and nickel plate were made cathode and anode respectively. Aqueous solution of nickel sulphate was used as the electrolyte. To avoid burnt deposition, hydrogen per ion must be balanced and for this reason boric acid was added in the electrolyte solution. Power supply for the electroplating was 3V and 6A, and was allowed for 1 minute. Thickness of nickel coating was around 500 nm. Further, graphene was grown on the nickel coated samples by chemical vapour deposition technique. A schematic diagram of CVD is shown in figure1. The specimens were placed on a ceramic tray and kept inside the quartz tube. The gases present inside the quartz tube were evacuated by a pump and a vacuum of order 1.2×10^{-2} torr was maintained. Then the furnace was heated up to a temperature of 850 °C and the catalyser i.e. H_2 (20 sccm) was allowed to flow for nearly 45 minutes. This is done to avoid oxidation of wafer and to retain activeness of the surface to be coated intact. The furnace was maintained at that temperature to allow annealing of the nickel coating [3]. Then the precursor i.e. acetylene (C_2H_2) was allowed to flow for 20 minutes at 6 sccm along with H_2 (20 sccm) and finally, the system was allowed to cool. With cooling carbon solubility in nickel is decreases. So segregation of carbon atoms occur which results in the formation of graphene. Then the specimens were brought out of the quartz tube. These coated specimens were kept safely so that coating doesn't get hampered.

2.3 *Tribological Tests*
After coating, tribology tests were carried out on the graphene coated samples. For tribology test, Tribometer (DUCOM, Bangalore, make) was used. Ball on disc (dry sliding) test was performed on the samples. Ball or counter-material was made of bearing steel of diameter 6 mm. Before testing, both sample and counter-material were cleaned properly in acetone. In this test, normal load was kept constant at 1 N. Sliding distance was fixed at 100 m. Tests were conducted by varying the speed at 0.05 m/s, 0.075 m/s and 0.1 m/s on both coated and uncoated bearing steel samples. Tests were performed at room temperature. At initial stage a point contact was made between ball and the specimen. During the test, no interruptions were made. Also, as it was being carried out at atmospheric condition, temperature and humidity ratio, two influencing factor, can be assumed to be constant. After the wear test, friction data were collected by using WINDUCOM software. During tribology test it records the frictional force value occurring between specimen and counter-material. The average value of frictional force divided by the normal force gives the average value of the coefficient of friction.

A multi-functional tribo-meter (RTECH make) was used to analyse the surface texture of both coated and uncoated bearing steel samples. Several scanned images of samples were taken under white light. With the help of gwyddion and origin software, scanned images of worn tracks were analysed.

3. Characterisation

3.1 Raman Spectroscopy
Raman spectroscopy, is a light scattering technique and used for identification and characterization of graphene. Here, detected number of photons against Raman shift from incident laser gives the Raman spectrum. Raman spectra varies for material to material depending upon their vibrational mode [11]. In general, 'D' peak which occurs somewhere at around 1350 cm^{-1}, informs about modes of sp^2 carbon atoms actuation by presence of any defect structure. 'G' peak, graphitic region, which occurs at around 1580 cm^{-1}. 2D peak, 2^{nd} order disorder mode of carbon atom, occurs at around 2700 cm^{-1}[12]. This 2D peak gives the numbers of graphene layer [3].

The number of defects present in graphene layer can be found out by calculating intensity ratio of D and G band i.e. (I_D/I_G). It indicates the degree of graphitization. To find out the number of graphene layer, the intensity ratio of 2D band and G band i.e. (I_{2D}/I_G) need to be determined. High value of I_{2D}/I_G indicates about high quality and low number of graphene layers [3].

3.2 Scanning Electron Microscopy
HR SEM (NOVA NANO SEM) was used to investigate the topography of graphene coating on bearing steel samples. Because of tribology test, wear tracks were formed on the bearing steel specimens. To analyse wear behaviour, scanning electron microscopy was performed on those specimens. SEM (ZEISS) was used to analyse wear mechanism of worn out tracks on both graphene coated and uncoated bearing steel specimens.

4. Results and Discussion

Figure 2 shows the Raman spectrum of graphene coated bearing steel. From the observed peaks in figure 2, it is clearly evident that graphene has been grown on the nickel-plated bearing steel samples. By studying the intensity ratio of 2D peak to G peak, it can be confirmed that multilayer graphene has been formed.

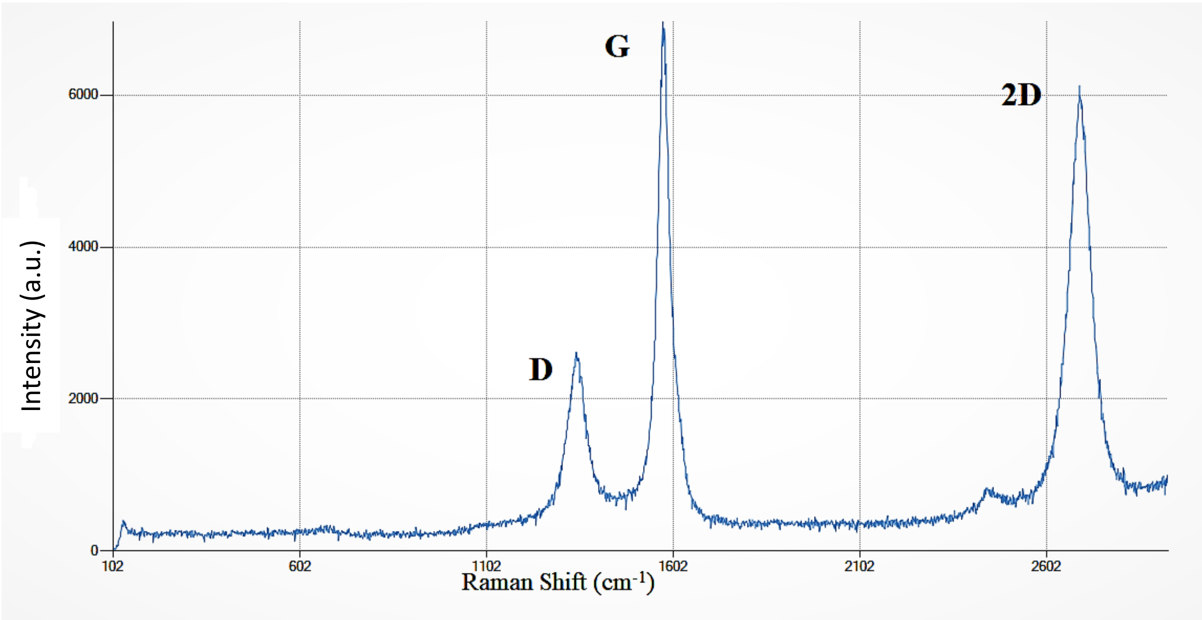

Figure 2. Raman spectrum of graphene

From figure 3(a) it can be observed the existence of few micro pores in the graphene layer. Further, it can be seen that graphene layers formed due to agglomeration of particles and they are interconnected to each other. Graphene layers have been stacked upon each other which indicates that monolayer graphene has not been formed, instead a multilayer graphene has been formed on nickel plated bearing steel. Uniformity in porous texture can be inferred from low magnification image as shown in figure 3(b).

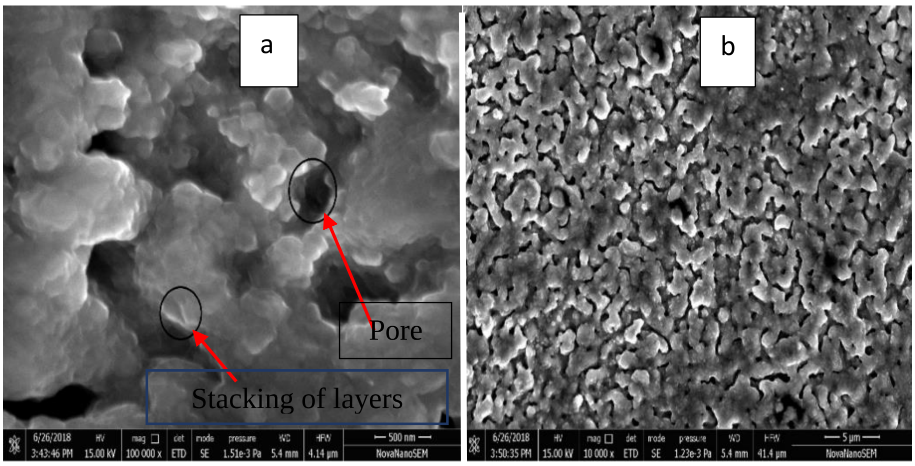

Figure 3. (a) HR SEM image of graphene (1,00,000×) **(b)** HR SEM image of graphene (10,000×)

From figure 4, it can be noted that the predominant modes of wear are abrasion and adhesion. Figure 4 (a) shows the direction of the sliding of counter material on the graphene coated surface. Because of mechanical action between two bodies, abrasion wear occurs which is shown in figure 4 (b). From that figure it can be observed that material has been displaced from the direction of movement of abradant creating a valley in that direction [13]. When the specimen and counter material i.e. ball are placed over each other and sliding action takes place, because of both the clean surfaces are in intimate contact, attractive force may cause localised bonding. This type of localised bonding may result in transfer of material. The worn-out material of the counter material smears on the surface of the specimen. This results in adhesive wear which is clearly shown in figure 4 (c).

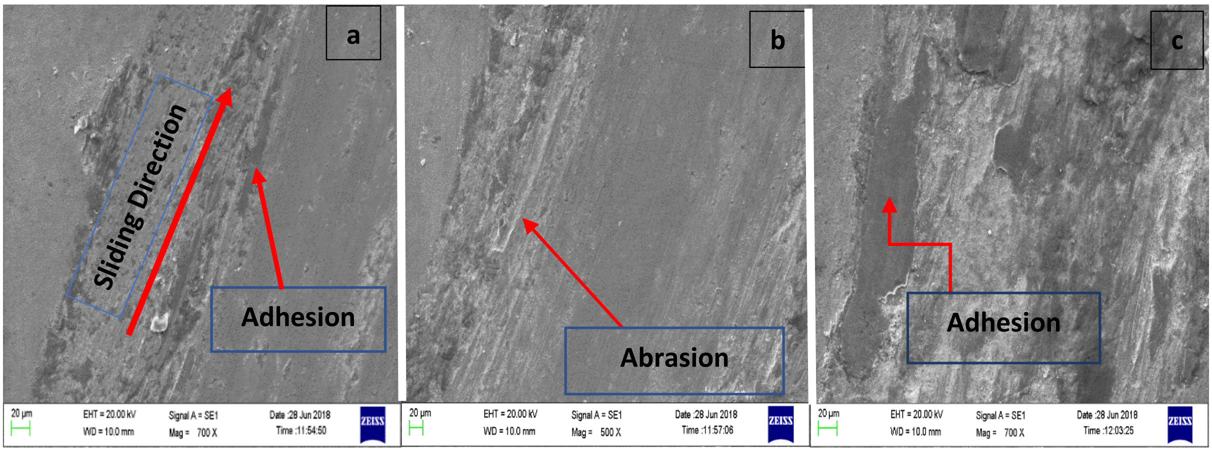

Figure 4. SEM images of worn track of graphene coated bearing steel **(a)** 0.05 m/s **(b)** 0.075 m/s **(c)** 0.1 m/s

Figure 5 shows the variation of co-efficient of friction (COF) with respect to sliding distance for the graphene coated and uncoated bearing steel material at a sliding speed of 0.05 m/s. From the figure it is clearly observed that co-efficient of friction of graphene coated material has reduced up to 3 times than that of the uncoated material. This can be attributed to excellent lubricating capability of graphene material.

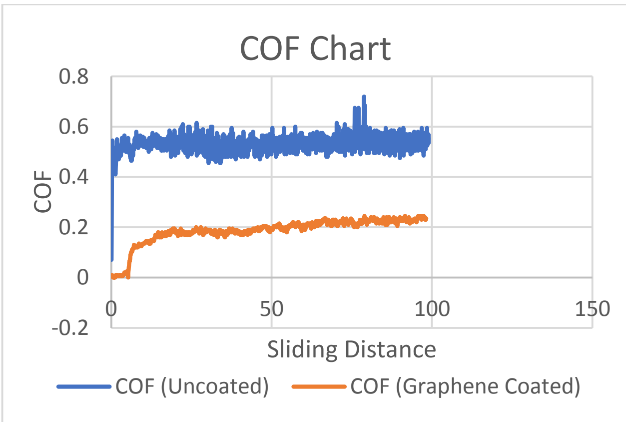

Figure 5. Variation of coefficient of friction (COF) in uncoated and graphene coated bearing steel material at 0.05 m/s

To find out the effect of sliding speed on co-efficient of friction, 3 different sliding speeds 0.05 m/s, 0.075 m/s and 0.1 m/s are selected and the results are shown in the figure 6. From the figure it can be observed that at all sliding speeds, coated material has less average COF than that of the uncoated one which shows the anti-friction characteristics of graphene. Further, it is observed that with increase in sliding speed, average co-efficient of friction is decreasing for graphene coated material, though the change is not significant. This is due to the presence of transfer layer of counter-material at higher speed. Also, with increase in speed, asperities present on the surface diminish, making the surface smoother. This may lead to reduction in friction.

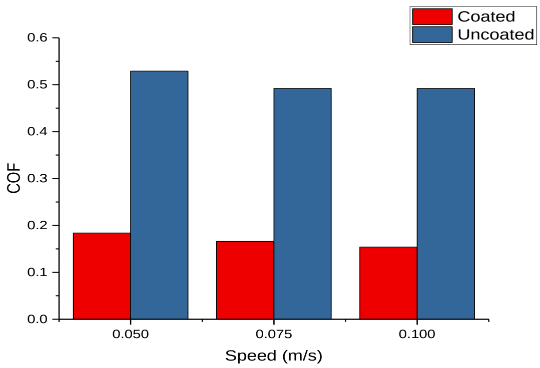

Figure 6. Variation of average COF at different speeds for both graphene coated and uncoated bearing steel

Wear rate analysis of bearing steel with graphene coating and without coating is shown in figure 7. It has been observed that wear rate of graphene coated material is much lower than that of the uncoated bearing steel. The wear rate of coated material is almost 0.2 times of the uncoated material. Also, it can be observed that with increasing the sliding speed, wear rate is decreasing for graphene coated samples. The chances of frictional heating amplify with increasing the sliding distance. The worn-out material then smears onto the surface of the coated sample because of frictional heating and mechanical action. So, this material layer now act like a protective layer over the coating surface. This is the reason for less wear of coated samples at higher speed.

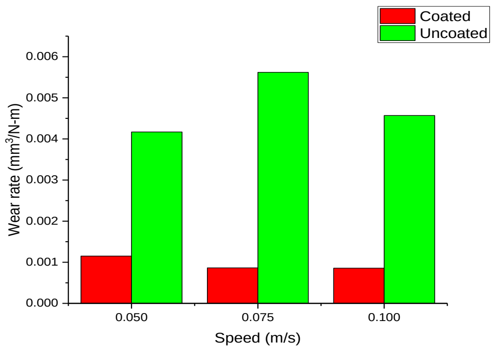

Figure 7. Variation of wear rate at different sliding speeds for graphene coated and uncoated bearing steel

5. Conclusions

From the above results and discussion the following conclusions can be drawn:

1. Graphene growth was carried out successfully by CVD technique on bearing steel samples.
2. With respect to uncoated bearing steel, graphene coated bearing steel has better tribological properties.

3. Coefficient of friction of graphene coated material has been reduced up to 200 % than that of the uncoated material.
4. Wear rate of graphene coated material has reduced up to 400 % than that of the uncoated material.
5. With increasing the sliding speed, the average value of coefficient of friction of graphene coated bearing steel decreases.
6. The wear rate decreases with increasing sliding speed for graphene coated bearing steel.

6. References

[1] Virendra Singh, DaehaJoung, Lei Zhai, Soumen Das, Saiful I Khondaker and Sudipta Seal 2011 Graphene based materials: past, present and future*, Progress in material science,* **56**, 1178-1271

[2] Praveen and Wani 2017 Synthesis and tribological properties of graphene: A review *JurnalTribologi* **13** pp.36-71

[3] M Prado Lavin-Lopez, Jose Luis Valverde, M Inmaculada Ruiz-Enrique, Luz Sanchez-Silva and Amaya Romero 2015 Thickness control of graphene deposited over polycrystalline nickel,*New J. Chem*. **39** 4414

[4] Francesco Bonaccoroso, Antonio Lombardo, TawfiqueHasan, Zhipei Sun, Luigi Colombo and Andrea C Ferrari 2012 Production and processing of graphene and 2D crystals *materials today* **15** pp. 564-589

[5] L Huang, Q H Chang, G L Guo, Y Liu, Y Q Xie, T Wang, B Ling and H F Yang 2012 Synthesis of high quality graphene films on nickel foils by rapid thermal chemical vapour deposition *Carbon* **50** pp. 551-556

[6] H Cheun Lee, Wei-Wen Liu, Siang-Piao Chai, Abdul Rahman Mohamed, Chin Wei Lai, Cheng-SeongKhe, C H Voon, U Hashim and N M S Hidaya 2016 Synthesis of single layer graphene: a review of recent development *Procedia Chemistry* **19** pp. 916-921

[7] Choon-Ming Seah, Siang-Piao Chai and Abdul Rahman Mohamed 2014 Mechanisms of graphene growthby chemical vapour deposition on transition metals *Carbon* **70** I-2I

[8] Bayram Yildiz, Arda Balkanci, Ismail Ovali and C Gökhan Ünlü 2018 Investigation of tribological behaviours of graphene-coated journal bearing T*ribology - materials, surfaces & interfaces* **12** pp. 177-185

[9] Philip Egberts, Gang Hee Han, Xin Z Liu, A T Charlie Johnson and Robert W Carpick 2014 Frictional behavior of atomically thin sheets: hexagonal-shaped graphene islands grown on copper by chemical vapor deposition *ACS Nano*. **8** pp. 5010–5021.

[10] M Reguzzoni, A Fasolino, E Molinari and M C Righi 2012 Friction by Shear Deformations in Multilayer Graphene *J. Phys. Chem. C* **116** pp. 21104–21108

[11] L M Malard, M A Pimenta, G Dresselhaus and M S Dresselhaus 2009 Raman spectroscopy in graphene *Physics reports* **473** pp. 51-87

[12] Reina, X Jia, J Ho, D Nezich, H Son, V Bulovic, M S Dresselhaus and K Jing 2009 Large area, few-layer graphene films on arbitrary substrates by chemical vapour deposition *Nano Lett.* **9** pp. 30-35

[13] Dewika Mishra, Farjana J Sonia, Dinesh Srivastava, G N Ganesha, Utpal Singha and Amartya Mukhopadhyay 2018 Wear damage and effects of graphene-based lubricants/coatings during linear reciprocating sliding wear at high contact pressure *Wear* **400-401** pp. 144-155