1. Introduction

Zinc carbon battery rods have been widely used for several applications, such as toys, remote control, radio and cameras. Every year battery waste increases. But the increase in the amount of battery waste is not balance with recycle processing of battery waste. Even though, carbon rod from waste of Zinc-Carbon battery contains Aluminum (Al) and Iron (Fe) which are harmful to human health and the environment [1–3]. Actually in modern batteries don't use Pb and Hg already in water. This will certainly endanger to human health [4, 5]. Good recycling of carbon batteries will contribute to improving environmental quality, but the amount of battery waste is not balance with decrease in the amount of battery waste [6–8]. Carbon atoms that have sp² hybridization have stronger bonds, so as to increase the hardness value of the thin layer of carbon material [7].

Previous research of carbon films were successfully synthesized using CVD plasma, hollow-cathode plasma and plasma sputtering [8]. Plasma sputtering has several advantages when compared to the other method, such as high deposition rate, low substrate temperature, and produce best quality thin film at lower substrate temperatures [10, 11]. Plasma sputtering bombards the target with energized particles, so that the ions from the carbon of the target material will come out and be deposited on the substrate. One of technique for carbon deposition in materials is low frequency 40 kHz plasma sputtering. The frequency is suitable for the plasma sputtering technique because the 40 kHz LFG generator has the highest ion density value of the two other plasma generator frequencies, 13.36 MHz and 2.45 GHz, so that more plasma particles are formed per square inch than...
generators others [11]. Changes of ion density cause changes in ion bombardment of the target material for deposition of thin films [8, 10].

One of gas that is suitable for use in plasma sputtering is argon gas. Argon is an inert noble gas, which means it will form very little or no chemical compounds. In argon gas the dominant influence in plasma sputtering is a physical reaction. Argon atoms are heavy atoms with low reactive properties, so it would be more effective if used to target materials for deposition of thin films [8, 11].

Recently, the use of steel as a material in the industrial world and machinery has developed rapidly. Steel in the market generally has limited mechanical performance. One example is SKD11 steel which only has a hardness of 58–60 HV [13]. Though SKD11 steel is widely used as dies, forming, and cutting so it requires high hardness performance [13, 14].

The highest chemical content of SKD11 steel is carbon (C) [15]. The hardness of steel can also be increased by increasing the carbon content of the steel [16]. One of the ways to increase carbon content can be done by coating the steel with amorphous carbon [17]. The amorphous carbon layer is attractive to researchers because of its good mechanical properties such as low coefficient of friction, hardness and high durability [18]. The hardness performance of SKD11 steel can be improved by deposition of an amorphous carbon layer by plasma sputtering process [19].

Previous research on deposition of carbon thin film on glass substrate using material target from battery carbon rods with plasma sputtering show that the carbon was successfully deposited onto glass substrate. It was proved by FTIR results, C–C and C=C was formed [1]. In the view of all these, argon plasma sputtering to deposition carbon thin film using material target from battery carbon rods may provide a new efficient approach to improve the mechanical properties of films. There is great scope to work on this topic further.

In the other studies, microstructural changes and hardness variations in SKD11 steel have been investigated during the processes of carbide dispersion (CD). However, the process of carbide dispersion carburizing requires high temperatures at 980 °C and the process takes a long time for 120 min. The process certainly requires a greater cost that plasma sputtering. Even though, plasma sputtering is more simple and cheaper than carburizing method to improve hardness performance of SKD11 steel. However, the investigation plasma sputtering process for hardening SKD11 steel was limited. On the other sides, SKD11 steel has limited hardness performance of 58–60 HV. Even though, the steel is commonly used for industrial purposes which require a high hardness performance. Therefore, studies that are devoted to obtain the maximum average of hardness value of carbon thin films on SKD11 steel with optimization of argon gas power parameter on plasma sputtering.

Based on these 3 methods, plasma sputtering has several advantages compared to other methods such as high deposition rates, low substrate temperatures, and synthesis high quality of thin films [8, 11]. Plasma sputtering works by utilizing high energy of plasma species as bombers of target materials [21].

Steel that is often used for industry, generally has limited mechanical performance. Many of research are done to improve steel mechanical performance [19]. One of the examples is research of increasing the hardness value of AISI H13 steel. The results of research indicate that increasing the hardness value with the increasing carbon content of AISI H13 steel [22]. Besides AISI H13 steel, there is steel that often used in the industrial world, such as SKD11 steel [23]. SKD11 steel is often used for dies, forming, and cutting [15]. However, SKD11 steel still has weaknesses. SKD11 steel has low hardness, around 58–60 HV [13]. Based on these problems, research has to do to increase the value of steel hardness. One of the ways is deposition carbon thin films on SKD11 steel with plasma sputtering.

Power is an important role in the process of plasma sputtering [19, 23]. The higher the power, the stronger the electric field that is formed, and the greater ion energy. If the energy of ion is greater than the binding energy of the target material's atoms, the atoms of the target material will be detached from the bonds of the atoms and move in all directions. The atom of the target material that comes out is called a sputtered atom [10]. Sputtered atom will be deposited on surface substrate and thin films structure that is formed will affect to the hardness of substrate [1].

A similar study about the effect of plasma sputtering RF power on diamond-like carbon thin films was previously had been carried out by Jongwannasiri et al. Based on the results of the study showed plasma treatment on DLC films surface influenced to thickness change, but not affect to structure of the films with various RF powers [24]. However, the limitation of this result didn't discuss about the effect of various plasma power on hardness of DLC films and only discuss the thickness of DLC films. Even though, Björling et al, found that the thicker deposited carbon thin film on substrate will have a high probability of carbon content [25]. In addition, Concepción et al, also found that the greater value of carbon content in carbon thin films, the greater value of hardness [16]. Therefore in this study, deposition carbon thin films with plasma sputtering for hardening SKD11 is done by using material target from battery carbon rods and determine effect power of plasma connected with hardness of carbon thin films on SKD11.

2. Literature review and problem statement

Plasma is the fourth phase form of matter after solid, liquid, and gas [20]. Plasma is formed due to ionization. Plasma can be applied as a method for deposition of thin films [12]. One application of carbon deposition is carried out on steel. Synthesis of thin films has been carried out using plasma enhanced chemical vapor deposition, plate parallel hollow cathode plasma with radio frequency, and plasma sputtering.

3. The aim and objectives of research

The aim of research is to investigate plasma sputtering process to increasing hardness of carbon thin films on SKD11 steel.

To achieve this aim, the following objectives are accomplished:

– to observe plasma power affected on hardness of carbon thin films on SKD11 steel.

4. Experimental method

4.1. Sample preparation

Material target that used in this research was prepared by carbon rod from zinc-carbon ABC battery waste
(ABC Battery Industry, made in Indonesia). The carbon rod was cut into reach diameter 8 mm and length 55 mm. Then, the carbon rod was cleaned by ultrasonication with 40 kHz and 360 W in soap, solution for 1 minute. The cleaned carbon rod was dried in the oven at 300 °C for 2 hours. The substrate used is SKD11 steel. Before plasma sputtering process, the substrate was cleaned by technical alcohol.

4.2. Deposition thin film

Carbon films were deposited using plasma sputtering. Plasma is generated by low frequency generator (LFG) 40 KHz. The plasma system has diameter chamber of 250 mm. The carbon rod as material target was placed at the electrode. The distance between the target material and SKD11 steel is kept at 1.7 cm. The argon gas was introduced with flow rate of 20 mL/min into the chamber after vacuum process of 1.5 hours. The power used for generation varies 300 W, 340 W, 380 W, 420 W and 460 W. The deposition is done for 2 hours, keeping the temperature at 300 °C. The illustration scheme of the plasma sputtering system used in this research is shown in Fig. 1 and plasma sputtering process on vacuum chamber shown in Fig. 2.

4.3. Characterization

The hardness value of SKD11 steel that has been deposited with carbon thin films on SKD11 with power treatment was tested using micro hardness Vickers at three different test points shown as Fig. 3. The hardness value of SKD11 steel is obtained by taking the average hardness value from measurements at three test points that have been done previously. The content and morphology of the carbon rod and thin films carbon on SKD11 steel with plasma sputtering treatment on optimum power parameters of 340 W was measured using scanning electron microscope/energy dispersive using X-ray (SEM-EDX).

5. Research results of hardness value of carbon thin films on SKD11 steel and SEM EDX

The hardness value of SKD11 steel that has been deposited with carbon film with power variations was tested with micro hardness Vickers to determine the effect of power on the plasma sputtering process on the hardness of SKD11 steel. The results of the SKD11 steel hardness test using micro hardness Vickers are shown in Table 1, Fig. 4.

| Test Point | Hardness Value (HV) Carbon thin films with Power |
|------------|--------------------------------------------------|
|            | 300 W    | 340 W    | 380 W    | 420 W    | 460 W    |
| 1          | 253.1    | 328.3    | 279.8    | 265.3    | 248.8    |
| 2          | 262.2    | 309.1    | 268.1    | 260.2    | 247.7    |
| 3          | 262.8    | 312.7    | 283.2    | 271.5    | 256.4    |
| Average of hardness | 259.3 | 316.7 | 277.0 | 265.7 | 251.0 |

The hardness value of carbon thin films on SKD 11 steel after power of plasma sputtering treatment based on the microhardness Vickers test

![Graph of hardness value of SKD11 Steel with power treatment](image-url)

SEM imaging of carbon rods and carbon thin film on SKD11 after plasma treatment with optimum power parameter of 340 W shown in Fig. 5, 6.
SEM observation was carried out on the outermost part of carbon rods from ABC battery waste shown as Fig. 5. The red line of Fig. 5 is an area that shows composition of battery carbon rods shown as Table 2. Based on SEM-EDX results shown as Table 2, atomic carbon level of carbon rods has 81.94%.

Table 2

| Element | Atomic % |
|---------|----------|
| C       | 81.94    |
| O       | 13.98    |
| Al      | 0.98     |
| Si      | 1.16     |
| Cl      | 0.54     |
| K       | 0.34     |
| Ca      | 0.43     |
| Fe      | 0.63     |

Fig. 5. SEM imaging of carbon rods outer layer from ABC battery waste

Table 3

| Compositions of carbon thin film on SKD11 steel after plasma sputtering treatment with optimum power parameter of 340 W based on SEM-EDX results |
|------------------------------------------------------------------------------------------------------------------------------------------|
| Element | Atomic % |
|---------|----------|
| Cr      | 15.76    |
| Mn      | 1.32     |
| Fe      | 54.51    |
| Ni      | 5.73     |
| Si      | 0.90     |
| O       | 8.32     |
| C       | 13.36    |
| V       | 0.11     |

6. Discussion of the research results of hardness value of carbon thin films on SKD11 steel and SEM EDX

Table 3 shown carbon purity level of thin film on SKD11 steel after plasma sputtering treatment with optimum parameter of 340 W.

It follows from Table 1 that the variation of power on plasma from 300 to 340 Watt increases the average of hardness value of carbon thin films on SKD11 steel, from 259.3 HV increased to 316.7 HV. However, power variations from 380 W, 420 W and 460 W have decreased hardness at 380 W to 460 W, from 277 HV to 251 HV. The treatment of power on plasma sputtering with highest average hardness value is obtained at power of 340 W with 361.7 HV. Fig. 4 shows that downturn on graph of relationship SKD11 steel with power treatment. Based on the graph shown as Fig. 4, the hardness value has a tendency to decrease when the power on plasma sputtering increases. This is because power is related to plasma energy. The greater the power causes the greater argon ion energy. It causes the transfer of energy from plasma to carbon atoms. As a consequence, carbon atoms have more energy when the power on plasma sputtering is greater. High-energy carbon atoms will tend to re-reflect or reflect rather than forming bonds or deposited on the surface. While at too low a power the carbon atom does not have enough energy to form carbon bonds on surface of SKD11 steel. At optimum power, the carbon atom is not too energetic but the energy it possesses is also not too small. As a result, the carbon bonds formed on the surface SKD11 steel are higher than the other power parameters. It can be seen in Fig. 7 which shows an illustration of the movement of carbon atoms from carbon rods on SKD11 steel substrates.

As follows from the Table 2 and Fig. 4, however, if this refers to previous research that solved the problem of successfully depositing carbon of carbon rod from waste of ABC battery which has 81.94% of atomic carbon on a glass substrate using plasma sputtering [1]. Based, on these results, the carbon of carbon rods from ABC battery waste has potential to be used as a target material for deposition of carbon thin films on SKD11 steel substrate.

Based on surface morphology, the outer surface of the carbon rod has a rougher shape than the outer surface of carbon thin films on SKD11 (Fig. 5, 6.). Based on the previous reference, the atomic carbon of SKD11 steel without treatment is 1.5%. Table 3 shows that if the atomic carbon of thin film on SKD11 after plasma treatment with optimum parameter of 340 W compared with the carbon con-
tent of SKD11 steel without treatment based on reference. Atomic carbon content in thin films on SKD11 with power treatment (13.36 %) is higher than atomic carbon content on SKD11 steels without treatment (1.5 %). Carbon impurities in thin films affect the value of hardness. High carbon impurities indicate that concentrations of atoms that are not same type are high. The higher carbon impurities deposited on SKD11 steel, cause more smaller possibility bonding between carbon and carbon on SKD11 steel. This bond is covalent bonds which is a strong bond and requires high energy to break the bond. More covalent bonds cause increasing the hardness of carbon thin films on SKD11.

The advantages of this research compared to the other similar research, studies that are more discuss the effect of LFG plasma sputtering power with hardness value of SKD11 steel and obtain the maximum average of hardness value of carbon thin films on SKD11 steel with optimization of argon gas power parameter on plasma sputtering. Previous research, about the effect of plasma sputtering RF power on diamond-like carbon thin films had been carried out. However, the limitation of this result didn’t discuss about the effect of various plasma power on hardness of DLC films and only discuss the thickness of DLC films [25]. The other studies also have been carried out by deposition of carbon thin film with LFG plasma sputtering power treatment of 220 W, 260 W, 320 W, and 340 W on glass using battery carbon rods as target. But, the result only discuss about FTIR results of carbon sputtering with various power [1].

The shortcomings and restrictions of the research, SKD11 without treatment are not tested by micro hardness Vickers to determine the hardness value. So that comparison of the hardness value of SKD11 steel without treatment is based on previous research as references and SEM-EDX is only tested on the most optimum power parameters of 340 W. Plasma sputtering system in this study still uses manual systems and there are no pressure gauge sensors of plasma sputtering system.

There are several things that can be developed in this research. Increased range of power variations (100–500 W) and measure the hardness value for each power variations. Pressure gauge can be added to know the value of pressure in the chamber of plasma sputtering system.

7. Conclusion

Experiment study of deposition carbon thin film on SKD11 with power on plasma sputtering treatment had been investigated to determine hardness performance. Based on micro hardness test, the optimum power treatment obtained at 340 Watt with the highest average hardness value is 316.7 HV. At optimum power, the carbon atom is not too energetic but the energy it possesses is also not too small. Based on SEM-EDX observation, it can be described that comparison of atomic carbon from carbon rods without treatment (1.5 %) and carbon thin films on SKD11 with optimum power treatment (13.36 %) show different value. Number of atomic carbon of thin films on SKD11 with power treatment is higher than atomic carbon of carbon rods without treatment.

References

1. Purkuncoro, A. E., Santjojo, D. J. D. H., Irawan, Y. S., Soenoko, R. (2019). Deposition of Carbon Thin Film by Means of a Low-Frequency Plasma Sputtering Using Battery Carbon Rods as a Target. IOP Conference Series: Materials Science and Engineering, 515, 012041. doi: https://doi.org/10.1088/1757-899x/515/1/012041
2. Klotz, K., Weistenbüler, W., Neff, F., Hartwig, A., van Thriel, C., Drexler, H. (2017). The Health Effects of Aluminum Exposure. Deutsches Ärzteblatt Online, 114 (39), 653–659. doi: https://doi.org/10.3238/arztebl.2017.0653
3. Tanong, K., Blais, J.-F., Mercier, G. (2014). Metal Recycling Technologies for Battery Waste. Recent Patents on Engineering, 8 (1), 13–23. doi: https://doi.org/10.2174/1872212108666140204004041
4. Nindhia, T. G. T., Surata, I. W., Atmika, I. K. A., Negara, D. N. K. P., Artana, I. P. G. (2015). Processing Carbon Rod from Waste of Zing-Carbon Battery for Biogas Desulfurizer. Journal of Clean Energy Technologies, 3 (2), 119–122. doi: https://doi.org/10.7763/jocet.2015.v3.179
5. Nindhia, T. G. T., Surata, I. W., Atmika, I. K. A., Negara, D. N. K. P., Artana, I. P. G. (2015). Processing Carbon Rod from Waste of Zing-Carbon Battery for Desulfurizer. Journal of Clean Energy Technologies, 3 (2), 119–122. doi: https://doi.org/10.7763/jocet.2015.v3.179
6. Erdemir, A., Donnet, C. (2006). Tribology of diamond-like carbon films: recent progress and future prospects. Journal of Physics D: Applied Physics, 39 (18), R311–R327. doi: https://doi.org/10.1088/0022-3727/39/18/r01
7. Chu, P. K., Li, L. (2006). Characterization of amorphous and nanocrystalline carbon films. Materials Chemistry and Physics, 96 (2-3), 253–277. doi: https://doi.org/10.1016/j.matchemphys.2005.07.048
8. Mori, T., Sakurai, T., Sato, T., Shirakura, A., Suzuki, T. (2016). Growth process of hydrogenated amorphous carbon films synthesized by atmospheric pressure plasma enhanced CVD using nitrogen and helium as a dilution gas. Japanese Journal of Applied Physics, 55 (4), 045503. doi: https://doi.org/10.7567/jjap.55.045503
9. Wen, F., Liu, J., Xue, J. (2017). The Studies of Diamond-Like Carbon Films as Biomaterials: Review. Colloid and Surface Science, 2 (3), 81–95.
10. Abdelrahman, M. M. (2015). Study of Plasma and Ion Beam Sputtering Processes. Journal of Physical Science and Application, 5 (2). doi: https://doi.org/10.17265/2159-5348/2015.02.007
11. Plasma Technology (2007). Available at: https://pdf.directindustry.com/pdf/diener-electronic/plasma-technology-diener-electronic/50802-410101.html
12. Hammadi, O. (2015). Fundamentals of Plasma Sputtering. Nanophotonics and Nanodevices Fabricated by Magnetron Sputtering Technique. doi: http://doi.org/10.13140/RG.2.1.3855.5605
13. General Catalog of YSS Tool Steels (2015). Available at: https://www.hitachi-metals.co.jp/e/products/auto/ml/pdf/yss_tool_steels_d.pdf
14. Yu, Z., Wang, Z. G., Yamazaki, K., Sano, S. (2006). Surface finishing of die and tool steels via plasma-based electron beam irradiation. Journal of Materials Processing Technology, 180 (1-3), 246–252. doi: https://doi.org/10.1016/j.matprotec.2006.06.014
15. Kong, J. H., Sung, J. H., Kim, S. G., Kim, S. W. (2006). Microstructural Changes of SKD11 Steel during Carbide Dispersion Carburizing and Subzero Treatment. Solid State Phenomena, 118, 115–120. doi: https://doi.org/10.4028/www.scientific.net/ssp.118.115
16. De la Concepción, V. L., Lorusso, H. N., Svoboda, H. G. (2015). Effect of Carbon Content on Microstructure and Mechanical Properties of Dual Phase Steels. Procedia Materials Science, 8, 1047–1056. doi: https://doi.org/10.1016/j.ijmpro.2015.04.167
17. Calik, A., Duzgun, A., Sahin, O., Ucar, N. (2010). Effect of Carbon Content on the Mechanical Properties of Medium Carbon Steels. Zeitschrift Für Naturforschung A, 65 (5), 468–472. doi: https://doi.org/10.1515/zna-2010-0512
18. Jones, B. J., Anguilano, L., Ojeda, J. J. (2011). Argon plasma treatment techniques on steel and effects on diamond-like carbon structure and delamination. Diamond and Related Materials, 20 (7), 1030–1035. doi: https://doi.org/10.1016/j.diamond.2011.06.004
19. Mróz, W., Burdyńska, S., Prokopuk, A., Jedyniński, M., Budner, B., Korwin-Pawłowski, M. L. (2009). Characteristics of Carbon Films Deposited by Magnetron Sputtering. Acta Physica Polonica A, 116, S-120–S-122. doi: https://doi.org/10.12693/aphyspol-a.116.s-120
20. Miyamoto, K. (2000). Fundamentals of Plasma Physics and Controlled Fusion. Available at: http://people.physics.anu.edu.au/~jnh112/AIM/c17/Miyamoto.pdf
21. González, J. M., Bertran, E. (2013). Mechanical and Surface Characterization of Diamond-Like Carbon Coatings onto Polymeric Substrate. Available at: https://arxiv.org/ftp/arxiv/papers/1509/1509.08512.pdf
22. Telasang, G., Dutta Majumdar, J., Wasakar, N., Padmanabham, G., Manna, I. (2015). Microstructure and Mechanical Properties of Laser Clad and Post-cladding Tempered AISI H13 Tool Steel. Metallurgical and Materials Transactions A, 46 (5), 2309–2321. doi: https://doi.org/10.1007/s11661-015-2757-z
23. Aizawa, T., Fukuda, T. (2013). Oxygen plasma etching of diamond-like carbon coated mold-die for micro-texturing. Surface and Coatings Technology, 215, 364–368. doi: https://doi.org/10.1016/j.surfcoat.2012.07.095
24. Jongwannasiri, C., Watanabe, S. (2014). Effects of RF Power and Treatment Time on Wettability of Oxygen Plasma-Treated Diamond-like Carbon Thin Films. International Journal of Chemical Engineering and Applications, 5 (1), 13–16. doi: https://doi.org/10.7763/ijcea.2014.v5.342
25. Björling, M., Larsson, R., Marklund, P. (2014). The Effect of DLC Coating Thickness on Elasto-Hydrodynamic Friction. Tribology Letters, 55 (2), 353–362. doi: https://doi.org/10.1007/s11249-014-0364-6