1. Introduction

The carbon in the carbon rod waste of zinc-carbon battery is a type of amorphous allotropy [1]. Amorphous carbon is an impure form of the element carbon. Besides, amorphous carbon has been widely used for various research and industrial purposes. This carbon can be used as a target material for thin film deposition on the material’s surface [2]. One of the applications of carbon thin film deposition is on steel [3]. The thin film of carbon has been carried out using the plasma-enhanced chemical vapor deposition method, plasma hollow-cathode, plate-parallel to radio frequency, and plasma sputtering. Among the three methods, plasma sputtering has several advantages over other methods, such as high deposition rate, low substrate temperature, and high quality of the synthesized layer [4].

Steel is a material that consists of essential elements, iron (Fe), and the primary alloy element, carbon (C). The carbon element’s primary function in steel is a material hardener by preventing the displacement of the dislocation in the iron atom’s crystal lattice [5]. Similar research has previously been carried out by adding carbon elements to increase steel hardness’s mechanical properties [6]. One type of steel that is often used in the industrial world is SKD11 steel [7]. The deposition of a thin layer of carbon using the plasma sputtering method on the SKD11 steel material is expected to increase the steel’s hardness value [3].

Carbon thin films on SKD11 steel were deposited by 40 kHz frequency plasma sputtering technique using a waste of battery carbon rods in argon plasma, and their mechanical properties were investigated by various target-substrate distances (1 cm, 1.7 cm, 2 cm, and 2.4 cm). The power used is 340 watts, the vacuum time is 90 minutes, and the gas flow rate is 80 ml/minute. The deposition time of carbon in plasma sputtering is 120 minutes with the initial temperature (temperature during vacuum) of 28 °C and the final temperature (the temperature after plasma sputtering) is 300 °C. The hardness value of SKD11 steel deposited with carbon thin films on SKD11 with target-substrate distance was tested using the Vickers microhardness test. Testing the thickness of the carbon thin films on the SKD11 steel substrate was carried out using a Nikon type 59520 optical microscope. Qualitative analysis of the thickness of the carbon thin films on the SKD11 steel substrate at a scale of 20 μm is shown by an optical microscope. Qualitatively, the thin film at a distance of 1.7 cm looks the brightest and thickest than other distance variations. Based on the Vickers microhardness test and Nikon type 59520 optical microscope, at the distance of 1 cm to 1.7 cm, the average thickness and hardness increased from 10,724 μm (286.6 HV) to 13,332 μm (335.9 HV). Furthermore, at the variation of the distance from 1.7 cm to 2.4 cm, the average thickness and hardness continued to decrease from 13,332 μm (335.9 HV) to 7,257 μm (257.3 HV). The possibility of interrupting atoms colliding with argon atoms in inert conditions increases at a long distance, thus causing the deposition flux on the SKD11 steel substrate to decrease.

Keywords: target-substrate distance, SKD11 steel, sputtering, hardness, thickness, carbon thin films
There are three main frequency ranges in plasma generation: 40 kHz (low frequency), 13.56 MHz, and 2.45 GHz (microwave frequency). The 40 kHz low-frequency generator has the lowest frequency of all frequency ranges. However, the 40 kHz low-frequency generator has the highest ion density value of the three plasma generator frequencies, which means that more plasma particles will be formed per square inch than other generators. The change in ion density causes a change in ion bombardment of the target material for thin film deposition. The 40 kHz low-frequency generator is more suitable for thin layer deposition using plasma sputtering [8]. Plasma sputtering can be generated with various types of gases. However, one of the gases suitable for use in plasma sputtering is argon gas [9]. Argon is an inert noble gas, which means the dominant influence in plasma sputtering is physics [10]. Argon atoms are heavy atoms with low reactive properties; it is more effective if used to bombard target materials for thin layer deposition [11].

Plasma sputtering on thin-film deposition with the material target can be influenced by several parameters, such as power, gas flow rate, target-substrate distance, and substrate temperature [12]. One of the parameters that affect the deposited carbon thin film’s mechanical properties is the target-substrate distance. Previous research investigates the effect of target-substrate distance on the mechanical properties of amorphous carbon films by magnetron sputtering technique using a graphite target with argon plasma. These studies indicate that target-substrate distance affects the deposition flux, which affects ion bombardment [13].

Previous research on carbon films’ characteristics deposited at two different distances between the substrate and target has been done by magnetron sputtering. The results show that the carbon films deposited at a target-substrate distance of 500 mm are thicker than those deposited at 100 mm. It indicates that target-substrate distance affects the thickness of the deposited carbon film on the substrate. However, the research only investigated two target-substrate distance variations, 100 mm and 500 mm [11]. In the other paper, the studies about the deposition of high-density amorphous carbon films with various target-substrate distances (150, 280, and 400 mm) have been done by sputtering enhanced (electron-beam-excited plasma). The Raman shift of the a-C film at 150 mm shows lower intensity than that spectrum intensity at 400 mm. However, the research does not discuss the hardness value of amorphous carbon films deposited on the substrate [14]. Previous similar studies have been conducted by observing the effect of target-substrate distance on the structural and mechanical properties of amorphous carbon films by middle frequency pulsed unbalanced magnetron sputtering technique using a graphite target in an argon plasma. These studies show that the film thickness increases with increasing target-substrate distance (40 to 50 mm) and decreases with increasing target-substrate distance (50 to 70 mm). The results indicate that target-substrate distance significantly influences the mechanical properties of amorphous carbon films deposited by middle frequency pulsed [13].

Based on previous research, the problem’s relevance is that no one has investigated the effect of target-substrate distance on the mechanical properties of carbon films deposited by 40 kHz low-frequency plasma sputtering using material target from carbon rods of zinc-carbon battery waste. The 40 kHz low-frequency generator produces a high ion density value, which means that more plasma particles will be formed per square inch than other generators. On the other hand, carbon rods from zinc-carbon battery waste can be reused as the target material for plasma sputtering to reduce battery waste pollution. Therefore, studies devoted to investigating the effect of target-substrate distance on the hardness properties of carbon film with 40 kHz low-frequency plasma sputtering using material target from zinc-carbon battery waste are of scientific relevance.

2. Literature review and problem statement

Steel consists of the primary constituent elements, iron (Fe), and the primary alloying element, carbon (C). According to the grade, an element of carbon in the steel ranges from 0.2% to 2.1% by weight. The carbon element in steel functions to improve steel's hardness performance by inhibiting the shift of dislocations in the crystal lattice of iron atoms [5]. The addition of carbon to steel can improve hardness performance, thereby improving the mechanical quality of industrial equipment made of steel [6].

One of the steels that are often used in industrial equipment is SKD11 steel. SKD11 steel is often used for making knife tips, scissors, and saw blades. Generally, SKD11 steel is used as a cutting tool. It requires high hardness performance [15]. One of the methods that can be used to increase the hardness of SKD11 steel is by adding carbon to the steel [16]. Similar research has previously been carried out by adding elemental carbon to increase carbon steel’s hardness properties. However, this study only discusses the effect of carbon content on the hardness properties of steel. It has not discussed the relationship between the thickness and impurity of carbon thin films [3, 6].

SKD11 steel has a chemical composition with various constituent elements, carbon (C), chromium (Cr), molybdenum (Mo), silicon (Si), manganese (Mn), and vanadium (V). The element carbon has a chemical composition (%) less than the element chromium. The carbon content is only 1.40 to 1.6%. It needs to be an increase in the carbon content of SKD11 steel to increase the material's hardness. The carbon element in steel serves to increase strength and hardness. Another element, molybdenum, can increase corrosion resistance and high temperatures. The chromium element, which is the most content in SKD11 steel, serves to increase oxidation resistance. The element silicon is used as an oxidizing agent in steel smelting, as most steels generally contain a small percentage of silicon. The addition of manganese to SKD11 steel can improve heat resistance, strength, toughness, and hardness [19].

The paper about the effect of target-substrate distance on the structural and mechanical properties of amorphous carbon films by middle frequency pulsed unbalanced magnetron sputtering technique using a graphite target in an argon plasma has been done. Research shows that the film thickness increases with increasing target-substrate distance (40 to 50 mm) and decreases with increasing target-substrate distance (50 to 70 mm). The results indicate that target-substrate distance significantly influences the mechanical properties of amorphous carbon films deposited by middle frequency pulsed. However, there were unresolved issues related to carbon film deposition with 40 kHz low-frequency plasma sputtering using material target from carbon rods of zinc-carbon battery waste. Furthermore, the study uses a variation of the target-substrate distance in an extensive range (40, 50, 60, and 70 mm). It is necessary to investigate target-substrate distance variations in a smaller range than at the target substrate distance in this study, such as 1, 1.7, 2
and 2.4 cm. The study only used middle frequency pulsed and did not use a 40 kHz low-frequency plasma generator [15]. The possible reason is that at low frequencies, 40 kHz is more challenging to form plasma sputtering than compared to middle frequency. However, the 40 kHz low-frequency generator has the highest ion density value of the three plasma generator frequencies, which means that more plasma particles will be formed per square inch than other generators. The 40 kHz low-frequency generator is more suitable for thin layer deposition using plasma sputtering than middle frequency [8]. All this suggests that it is advisable to conduct a study on the effect of target-substrate distance on thickness and hardness of carbon thin films on SKD11 substrate with 40 kHz low-frequency plasma sputtering using material target from carbon rods of zinc-carbon battery waste.

3. The aim and objectives of the study

The aim of the study is to investigate the effect of various target-substrate distances of 40 kHz plasma sputtering on the thickness and hardness of carbon thin films. The practical use of the results can increase the hardness of SKD11 steel in the industry because SKD11 steel in the industry is used to manufacture cutting tools, which requires high hardness performance.

To achieve this aim, the following objectives are accomplished:

- to investigate the effect of various target-substrate distances of 40 kHz plasma sputtering on thickness and hardness of carbon thin films;
- to observe the relationship between the thickness and hardness of carbon thin films on SKD11 steel on various target-substrate distances.

4. Experimental method

4.1. Sample preparation

This research’s material target was prepared by a 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 35 mm. The carbon rod was then cleaned by the ultrasonic cleaner 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 the plasma sputtering process, the substrate was cleaned with technical alcohol.

4.2. Deposition of thin film

The carbon thin film is deposited using 40 kHz low-frequency plasma sputtering. The plasma system has a chamber diameter of 250 mm. The carbon target material from the zinc-carbon battery waste carbon rod is placed between the electrodes. The distance between the target material and the SKD11 steel substrate was carried out with variations of 1 cm, 1.7 cm, 2 cm and 2.4 cm. The power used is 340 watts, the vacuum time is 90 minutes, and the gas flow rate is 80 ml/minute. The deposition time of carbon in plasma sputtering is 120 minutes with the initial temperature (temperature during vacuum) of 28 °C and the final temperature (the temperature after plasma sputtering) is 300 °C. The illustration scheme of the plasma sputtering system used in this research is shown in Fig. 1. The components of the tool in the plasma sputtering system shown in Fig. 1 are as follows:

1. 40 kHz Diener low-frequency generator (LFG) serves to generate plasma in the system.
2. The vacuum pump functions to create a vacuum in the plasma chamber, thereby facilitating plasma formation in the chamber.
3. Thermocouple functions to adjust the temperature of the substrate in the plasma sputtering system.
4. Flowmeter functions to regulate the flow rate of argon gas in the plasma sputtering system.
5. The adjustable distance is used to adjust the target-substrate distance.

The plasma sputtering process on the vacuum chamber for carbon thin films deposition is shown in Fig. 2.

During the plasma sputtering process, argon plasma formed as shown in Fig. 2.
4.3. Characterization of thin film

The hardness value of SKD11 steel deposited with carbon thin films on SKD11 with power treatment was tested using Vickers microhardness test at three different test points shown in 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.

Testing the thickness of the carbon thin films on the SKD11 steel substrate was carried out using a Nikon type 59520 optical microscope shown in Fig. 4. Before characterization with the Nikon Type 59520 optical microscope, the sample was placed on the surface of the resin as shown in Fig. 4.

Resin preparation aims to determine the boundary area between SKD11 steel, deposited carbon thin films, and resin at the time of optical microscopy characterization. The sample was placed on the preparation table shown in Fig. 4. The magnification was set at 200x. The observed data were then processed with the Nikon optical microscope type 59520 software, and the thickness values were obtained at three different points.

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

5.1. Thickness of carbon thin films on the SKD11 steel substrate at the variation of target-substrate distance

The thickness and the hardness value of carbon thin films on SKD11 steel with target-substrate variations were tested with the Nikon type 59520 optical microscope and Vickers microhardness test. The thickness results of carbon thin films using the Nikon type 59520 optical microscope are shown in Fig. 5–8.
Quantitative data of thickness values of carbon thin films on SKD 11 steel at 1 cm, 1.7 cm, 2 cm, and 2.4 cm target-substrate distance based on the Nikon type 59520 optical microscope are presented in Table 1.

| No. | Target-substrate distance (cm) | Thickness point (μm) | Average (μm) |
|-----|--------------------------------|----------------------|--------------|
| 1   | 1                              | 12.178               | 10.867       |
| 2   | 1.7                            | 13.040               | 13.482       |
| 3   | 2                              | 11.301               | 8.693        |
| 4   | 2.4                            | 6.534                | 7.257        |

The graph of average thickness values of carbon thin films on SKD11 steel at various target-substrate distances (1, 1.7, 2 and 2.4 cm) is shown in Fig. 9.

The relationship between variations of the target-substrate distance and the average hardness of the carbon layer on the SKD11 steel substrate is plotted in the graph, as shown in Fig. 10.

| Test point | Hardness value of carbon thin films on the SKD11 substrate at various target-substrate distances (HV) |
|------------|--------------------------------------------------------------------------------------------------|
| 1 cm       | 293.60 379.90 267.4 261.6                                                                        |
| 2 cm       | 273.60 321.60 252.9 256.4                                                                         |
| 3 cm       | 292.60 306.30 265 254.1                                                                             |
| Average    | 286.6 335.9 261.7 257.3                                                                             |

5.2. Hardness value of carbon thin films on the SKD11 steel substrate at the variation of target-substrate distance

Based on the hardness value test results using the Vickers microhardness test, the distance variations are shown in Table 2.

The relationship between the average thickness and the average hardness of the carbon thin films on the SKD11 steel substrate at various target-substrate distances is shown in Fig. 11.

Based on Fig. 11, the relationship between the average thickness and the average hardness shows a non-linear pattern relationship. At the target-substrate distance of 1 cm to 1.7 cm, the average thickness and hardness value increases. However, at the target-substrate distance of 1.7 cm to 2.4 cm, the average thickness and hardness value decreases.
6. Discussion of the research results of thickness and hardness value of carbon thin films on SKD11 steel

Qualitative analysis of the thickness of the carbon thin films on the SKD11 steel substrate at a scale of 20 μm shown by an optical microscope in Fig. 5–8 visually observed the carbon thin films formed on the SKD11 steel surface, which is indicated in white. Qualitatively, the thin film at a distance of 1.7 cm looks the brightest and thickest than other distance variations. Meanwhile, the thin layer at a distance of 2.4 cm looks qualitatively the thinnest and darkest than other distance variations. It is supported by the data in Table 1, at a distance of 2.4 cm, the average value of carbon layer thickness is 7.25 μm, which is the lowest thickness value compared to other distance variations.

Similar research has previously been carried out by observing the effect of the distance of the target material (40, 50, 60, and 70 mm) on the thickness of the amorphous carbon thin films formed on the glass after 2 hours of plasma sputtering process with 290 W power and 40 kHz generator. The results showed that the higher the distance between the target material and the substrate, the thinner the film's thickness would decrease. At a short distance between the target material and the substrate, re-sputtering occurs and there is the possibility of increased deposition flux on the substrate [13]. Table 1 and the graph in Fig. 9 show a decreasing pattern at a target-substrate distance from 1 cm to 2.4 cm. At a distance of 1 cm to 1.7 cm, the average thickness value increases from 10.724 μm to 13.332 μm; this is because, at a short distance, there is little chance of the interrupted atoms colliding with the argon atom in an inert condition; this causes a deposition flux against it. SKD11 steel substrate is increased. At a target-substrate distance from 2 cm to 2.4 cm, it shows a decrease in the average value of the thickness of the carbon layer from 10.145 to 7.257 μm. Based on previous references, Dai and Zhan (2015), it can be used as a basis for explaining the effect of the distance between the target material and the substrate on the thickness of the deposited carbon thin film. If the substrate is far away from the target, the target material’s sputtered particles undergo more collisions with inert argon atoms. This may lead to loss of deposition flux [13].

The relationship between average thickness and average hardness of the carbon layer on the SKD11 steel substrate with variations in the distance between the target material and the substrate is shown in Fig. 11. At the variation of the distance of 1 cm to 1.7 cm, the average thickness and hardness increased from 10.724 μm (286.6 HV) to 13.332 μm (335.9 HV), as shown in Table 2 and Fig. 10. Furthermore, at the variation of the distance from 1.7 cm to 2.4 cm, the average thickness and hardness continued to decrease from 13.332 μm (335.9 HV) to 7.257 μm (257.3 HV). Based on previous references, Dai and Zhan (2015) investigate the effect of target-substrate distance on the structural properties of amorphous carbon films. The result of X-ray photoelectron experiments shows that the ratio of sp3/sp2 in amorphous carbon films increases with increasing target-substrate distance from 40 to 60 mm, and then decreases at 60 to 70 mm. If the ratio of sp3/sp2 in amorphous carbon films increases, there are more bonds between the carbons (covalent bonds). It causes an increase in the hardness value of carbon thin films. In previous research, Dai and Zhan (2015), there is a possibility that at a distance of 1.7 cm, which is the variation of the distance with the highest value of thickness and hardness of the carbon layer because the ratio sp3/sp2 in the carbon layer is the highest, the hardness value is the highest when compared to other distances [13].

Compared to the other similar research, this research’s advantages discuss the effect of target-substrate distance on the thickness and hardness value of carbon thin films on SKD11 steel by 40 kHz plasma sputtering. Previous similar studies have been conducted by observing the effect of target-substrate distance on the structural and mechanical properties of amorphous carbon films by middle frequency pulsed unbalanced magnetron sputtering technique using a graphite target in an argon plasma. These studies show that the film thickness increases with decreasing target-substrate distance (40 to 50 mm) and decreases with increasing target-substrate distance (50 to 70 mm). The results indicate that target-substrate distance significantly influences the mechanical properties of amorphous carbon films deposited by middle frequency pulsed [13]. However, this result’s limitation does not discuss the effect of target-substrate distance on the thickness and hardness value of carbon thin films on SKD11 steel using carbon rods of battery waste as a material target by 40 kHz plasma sputtering.

The shortcomings and restrictions of the research, SKD11 without treatment, are not tested by the Vickers microhardness test. Therefore, the value of hardness without treatment as a control variable and hardness with distance treatment could not be compared. The plasma sputtering system in this study still uses manual systems, and there are no pressure gauge sensors of the plasma sputtering system. Several things can be developed in this research. Increased range of target-substrate variations (2.5–4 cm) and measure the hardness value for each target-substrate variation. A pressure gauge can be added to know the value of pressure in the chamber of the plasma sputtering system.

7. Conclusions

1. The thickness and hardness of carbon thin films increased from 1 cm to 1.7 cm, the average thickness and hardness increased from 10.724 μm (286.6 HV) to 13.332 μm (335.9 HV). Furthermore, decreases with further increasing target-substrate distance from 1.7 cm to 2.4 cm, the average thickness and hardness continued to decrease from 13.332 μm (335.9 HV) to 7.257 μm (257.3 HV).
2. At target-distance variation in plasma sputtering, the increasing thickness of carbon thin films increases carbon thin films’ hardness. With the thickness of 7.257 μm, the hardness value is 257.3 HV; 10.145 μm, the hardness value is 261.7 HV; 10.724 μm, the hardness value is 286.6 HV and 13.332 μm, the hardness value is 335.9 HV. The highest thickness and hardness values of carbon thin films were obtained at a distance of 1.7 cm, 13.332 μm and 335.9 HV.

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