The role of nanocatalyst of pearl oyster shell in pack carburizing process on mechanical and physical properties of AISI 1020 steel

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Abstract. The most commonly used metal material in the industry today is steel. Steel is classified based on its carbon content. There are high-carbon steel, medium-carbon steel, and low-carbon steel. The steel used in this research is low-carbon steel, namely AISI 1020 steel, with a carbon content of around 0.1% to 0.3%. With a low-carbon content, the hardness is also low. Pack carburizing is carried out to overcome this issue. The media used are coconut shell nanocarbon and pearl oyster shell nanocatalyst. Specimens were made with a mixture of nanocatalyst variations given around 0%, 10%, 20%, and 30% with the use of 900º C temperature with a holding time of 60 minutes. Preparation of nano-sized media using the High Energy Milling (HEM) process using a shaker mill machine. The treated specimens were then subjected to Vickers hardness testing with 5 kg and 200 gf loading, microstructure observation, and FTIR observation. The highest Vickers macro hardness test was obtained through the 20% nanocatalyst variation, resulting in a hardness value of 255 HV. The increase that occurred compared to without treatment increased by 91%. Then the micro Vickers hardness testing resulted in a value of 399 HV. The resulting microstructure is evenly distributed pearlite grains and gradations of ferrite grains. The carburizing depth is achieved optimally through a 20% variation of pearl clam shell nanocatalyst, with a depth of ± 0.19mm. Then FTIR observation also shows the presence of new groups of vinylidene-type alkene compounds. These compounds are flammable and volatile, so they can provide additional energy in the pack carburizing process.

1 Introduction

1.1 Background

A high-value component in sophisticated equipment must have proper working requirements, especially in the aerospace, nuclear, marine, and other industries. Steel is a metal material that is currently often used in the industrial world with its various advantages. It has iron as the fundamental element and carbon as the main element. Steel is classified based on its carbon content. One of the steel classifications is low-carbon steel, with a carbon content of

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around 0.1% to 0.3%. This research uses AISI 1020 steel, which is low-carbon steel. AISI 1020 steel is usually used for making gears. Because gears must withstand complex loads and a high risk of failure [1], a particular treatment, namely carburizing, is needed. Substantially, some samples' durability can be improved through carburizing heat treatment [2,3].

Through carburizing of low-carbon steel, capable of producing coating depths of up to 200 μm [4]. Pack carburizing is the treatment of the metal by heating at a specific temperature and holding time. Pack carburizing is simple and economical, so it is widely used by the industry [5]. It has been used to increase the hardness of the surface [6]. It is because the hardness value of the surface is essential to increase the performance of the part [7]. The modified surface layer generally has a gradient out microstructure, better known as a heterogeneous structure [8]. In the pack carburizing process, fast cooling is carried out at the final stage to prevent the carbon that has diffused from escaping back to the surface.

The increased hardness value of steel is due to additional media when the pack carburizing process [2]. The increase of this value can also be seen through the observation of microstructure. During observation, there is a change in microstructure in the surface area towards the core of the specimen [9].

Carbon in nano size is used for additional media in the pack carburizing process to increase the carbon ingredient in the steel. Coconut shell charcoal is usually used as additional media. The carbon content of coconut shell charcoal ranges from 78% [10].

Using nanocarbon as pack carburizing media still needs to provide optimal results to increase the hardness value of steel material. Catalysts can provide additional energy in the pack carburizing process [11]. The additional energy is expected to help the carburizing media push the carbon media to diffuse more into the steel core.

The widely used catalyst usually are Barium Carbonate ($BaCO_3$), Calcium Carbonate ($CaCO_3$), or Natrium Carbonate (Na_2CO_3). Catalysts derived from chemicals harm the environment and humans. Alternative catalyst media can be used from pearl oyster shells [12]. The utilization of pearl oyster shell waste is necessary to produce waste that can be utilized appropriately. One of the utilizations is through the high calcium carbonate ($CaCO_3$) content in pearl mussel shells, which is more than 90% [13].

The use of high-performance materials can improve performance. Therefore, it is necessary to advance industrial technology [14]. In the development of material science, it is possible to engineer nano-sized materials. Nano-sized materials range from 1-100 x 10-9 meters. Materials in nano size have more incredible surface energy than materials in micro size due to the larger surface area in the same volume.

Pack carburizing process with corn cob charcoal media and pearl oyster shell can affect the surface hardness value and the resulting microstructure. Through various mixtures, a 20% catalyst pearl oyster shell with a heating temperature of 950°C and a holding time of 150 minutes can provide optimum results. Hardness value obtained 262,27 kg/mm^2 [11].

The study of the pack carburizing process using nanocatalysts of pearl oyster shells has yet to be widely carried out. Therefore, this research will study the role of catalysts from pearl oyster shells as an additional medium in the pack carburizing process. Research related to the effect of variations from nanocatalysts given with a mixture of nanocatalysts from pearl oyster shells is expected to increase the hardness value on the surface of low-carbon steel with time efficiency with optimal results.

2 Research methods

2.1 Tools

Making test objects requires several tools and materials. The material used is low-carbon steel, AISI 1020. Pearl oyster shells are used as a catalyst or energizer in pack carburizing. Pearl oyster shell particle size is made in nanomaterial size. Then, coconut shell charcoal is used as an additional material in the pack carburizing process. Coconut shell charcoal is made in the form of nanomaterial-sized particles. Before the test specimens were given pack carburizing treatment, the test specimens were first given normalizing treatment. Normalizing aims to make the structure of the material return to its original structure at the beginning of production.

2.2 Materials

Two additional materials are given in the pack carburizing process, namely coconut shell charcoal as carbon and pearl oyster shells as catalysts. The initial ingredients are pieces, then ground until smooth [12]. Then put into the tube with an amount of 1/3 of the volume of the tube container, add a ball mill about 1/3 of the volume. A shaker mill machine with High Energy Milling (HEM) method was used. With two million shaking cycles, it is more than enough to manufacture nanoscale material [15]. The resulting nanocarbon is shown in the figure 1(a). The resulting nanocatalyst is shown in the figure 1(b). Both nano-sized additives must be stored in a closed container to not react with oxygen.

(a) **(b)**

Fig. 1. Carburizing media (a) Nanocarbon, (b) Nanocatalyst.

2.3 Pack carburizing process

AISI 1020 steel that has been given a normalising treatment can be processed pack carburising. The mixture variation between nanocatalyst and nanocarbon is mixed first in a separate container, then wrapped in sealed paper tightly and densely. Then the specimen, wrapped with carburising additives, can be put into a sealed pack carburising container. When the oven has reached the set temperature, the pack carburising container is put into the oven at 900° C with a holding time of about 60 minutes. The specimen is removed from the carburising container after the holding temperature and time are reached.

2.4 Specimen preparation

The first preparation is splitting the specimen because the test will be observed from inside the specimen. The process uses a precision cutting machine so that the cutting does not affect the structure. The specimen is gripped and turned on, and the machine will operate automatically.

Second, the specimens are moulded with resin so that specimens A, B, and C can be combined, and the following process is effective. Moulding with liquid resin is done manually with a mould container made of an aluminium sheet. The resin mixture was stirred manually for five minutes and poured into the mould. Before moulding, be sure to mark each specimen. Curing of the specimens takes place for 1x24 hours.

2.5 Polishing and grinding process

The polishing and grinding process uses a polishing machine, aiming that the surface of the specimen is flatter and smoother so that the microstructure observation is easier to observe and more precise. The grinding process uses sandpaper from levels 80, 100, 120, 200, 400, 600, 800, 1000, 1500, and 2000 using 250-400 rpm speeds. From each grinding level, it can be seen through the scratch produced in the same plane or direction. After reaching the final level, the polishing process can be continued by applying the metal polishing paste on a clean cloth and rubbing the specimen repeatedly until it looks shiny.

2.6 Microstructure observations

Microstructure observation is done throughout all species to know different about specimens without treatment or with treatment. Observation with an optic microscope uses M20/0.40 lens. Before observation, the first surface of the specimen is pre-dripped with etching liquid. With that liquid, the pores of each specimen will open. The liquid is 95% HNO_3 and 95% alcohol in a specific ratio, with a holding time of about 60 seconds, and the entire surface is covered. After completing, immediately clean the etching liquid to stop the corrosion process.

Observing the microstructure can also determine the carburising depth through the dominating area. The measurement method compares the photo of the area results with a photo of the copper wire microstructure, which is known to be the original size. Depth measurement needs to be done to develop further research so that the same method can produce a more optimal value.

2.7 Vickers hardness testing

Hardness testing is carried out macro and micro. For macro testing to find the basis for the highest hardness value of all specimens, further micro testing is carried out. The load is based on the type and composition of the specimen material. At macro, a load of 5 kg was given with a holding indentation time of 10 seconds. Vickers macro testing was carried out with a DHV-50D machine belonging to the metal science laboratory of Sanata Dharma University Yogyakarta. Data generated from macro testing in the form of indenter marks, which are then measured using a microscope from the machine. Each specimen received five tests with different points with a distance of $\pm$ 1mm between test distances.

Then in the Vickers micro test using a load of 200 grf with an indentation hold of 5 seconds, the test distance is 100 microns. The machine used is the Buehler-50D machine owned by the materials laboratory of the department of mechanical and industrial engineering Bachelor's Degree Gadjah Mada University. The data generated is also the same as

macroVickers, which is in the form of diagonal trampling results that can be measured through a machine microscope.

2.8 FTIR observations

Fourier Transform Infra-Red observations were used to simultaneously observe the infrared spectrum in all wave numbers. The media observed were nanocarbon, nanocatalyst, and various variations with the most optimal results. The sample was tested in the form of powder. To analyze the spectrum that occurs using computer applications, which will turn into spectrum measurements and peak detection. The results of the FTIR test will be matched manually with the previously available database by comparing the band absorbs with the correlation table and the comparison compound.

3 Discussion

3.1 Hardness test result

Hardness test results with specimens treated with pack carburizing and untreated specimens with variations in the composition of nanocatalyst media 0%, 10%, 20%, and 30%.
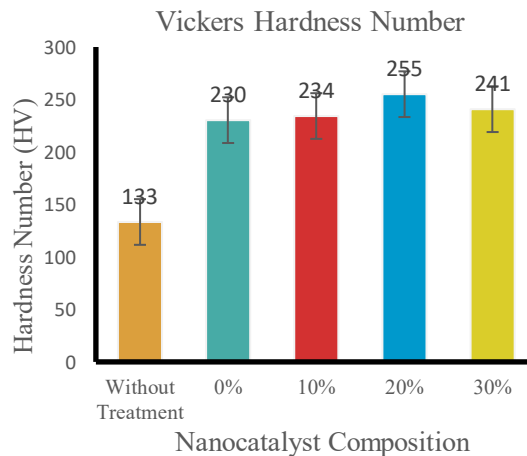

Fig. 2. Surface hardness number of AISI 1020 steel against nanocatalyst composition variation.

The increase in hardness number from 133.3 HV in specimens without carburizing treatment to 230.3 HV in specimens with 0% nanocatalyst. Then there was an increase again when given a nanocatalyst of 10% with a hardness value of 234.2 HV, with an increase from untreated specimens by 73%. Then the most optimal increase in hardness number was achieved by adding a nanocatalyst of 20% with a hardness value of 255 HV, with an increase from untreated specimens by 91%. From the comparison Figure 2, the untreated specimen has the lowest hardness. Pack carburizing, with the addition of media on the surface of the specimen, results in a higher surface hardness value. The diffusion of carbon atoms into the iron makes the formation of cementite, which consists of 3 Fe atoms by binding 1 C atom, making it $Fe_3 C$. This new bond will form cementite. The growth of new cementite will mix with ferrite to form new pearlite bonds. This pearlite bond has more complex properties than ferrite.

Temperature also affects the rate of diffusion of carbon atoms into the specimen surface. The higher temperature, the faster the diffusion process. The carburizing media mixture can

increase the formation of CO_2 from the nanocatalyst that decomposes, helping increase the formation of CO gas. This gas reacts to form carbon atoms and diffuses into the surface of the specimen. A 30% decrease in the hardness value of the nanocatalyst specimen resulted in 240.7 HV. Despite the decrease, there was still an increase of 80.5% compared to untreated. The decrease in hardness is due to the decreased capacity of carbon to react with carburizing. The amount of CO_2 gas and carbon availability does not allow it to be diffused into the surface. Then, microhardness testing is intended to determine the hardness mapping of the specimen from the surface to a certain depth. Testing is done through the most optimal macro hardness value. Testing from the edge of the distance of 0.5 mm to 1.0 mm with a range of 0.1 mm. The microhardness test results can be seen in Figure 3.

Vickers Micro Testing Number
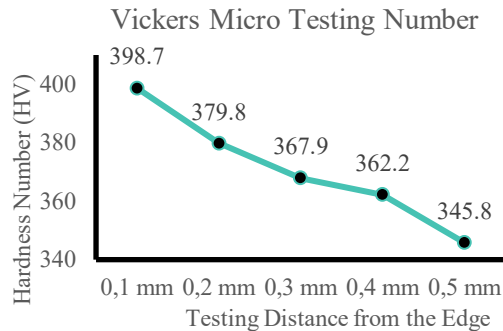
Fig. 3. Hardness number against distance from surface.

With the most optimal hardness value on the outside reaching 398.7 HV and the lowest hardness value of 345.8 HV, the surface that directly meets the carburizing media has a higher hardness number when compared to the inside of the specimen. Although the hardness value is not too far away, it still makes a hardness difference.
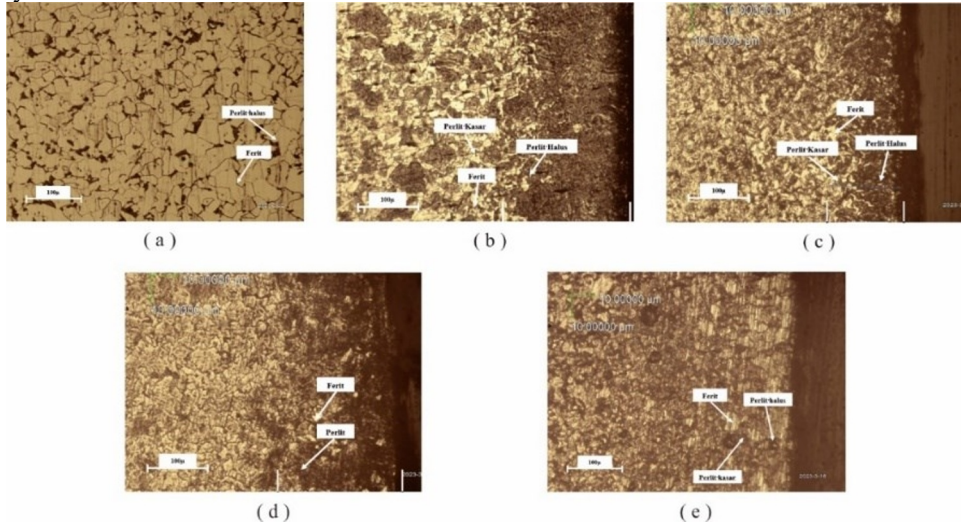
3.2 Microstructure observation result

Microstructure observations were made on specimens before and after pack carburizing treatment. The observed area is at the centre point of the specimen, with the aim that there is no influence of carbon diffusion from the side. The results of the microstructure observation can be seen in Fig. 4., specimen (a) was given a normalizing treatment. Using a temperature of 900° C with a holding time of 60 minutes. From the microstructure testing, the microstructure is obtained in the form of fine ferrite, fine pearlite, and coarse pearlite. Ferrite is visible in the image with a brighter colour, while the darker and denser colour is a pearlite structure, both fine pearlite and coarse pearlite. The size of the ferrite and pearlite structures is relatively uniform. With the dominant ferrite form rather than the pearlite form, it only has a medium hardness value.

The pearlite structure looks more dominant with a larger area with a solid colour, while the ferrite structure looks brightly coloured with less area. The pearlite structure looks more dominant due to the carbon diffusion process during the pack carburizing process. The pearlite crystal layer formed becomes more and more as the $CaCO_3$ nanocatalyst increases. This phenomenon can be observed in Figure 4 (a).

The amount of ferrite is more dominant in Figure 4 (e) compared to Figure 4 (b), but the hardness number in Figure 4 (e) is higher. This higger hardness number because the fine pearlite structure is more dominant in Figure 4 (e), while in Figure 4 (b), the fine pearlite structure is less. Figure 4 (d) has the highest hardness value, with a value of 255.0 HV. The high hardness value is because the pearlite structure has more than the others.

The pack carburizing process shows that the entire specimen area shows a more dominant black area than untreated specimens. This phenomenon shows that carbon atoms have diffused into the surface of AISI 1020 steel, passing through the grain boundary gap, filling the void in the Fe atom cavity, binding with Fe atoms, and forming cementite with a black layer.

Fig. 4. Micro structure obseration result (a) Without treatment, (b) 0% Nanocatalyst, (c) 10% nanocatalyst, (d) 20% Nano Catalyst, (e) 30% Nanocatalyst.

3.3 FTIR testing result

FTIR testing aims to determine a functional group in a test sample. Testing was carried out with powder samples, namely nanocarbon sample, nanocatalyst, and variations in carburizing media with the optimal result. The test results can be seen in Fig. 5.
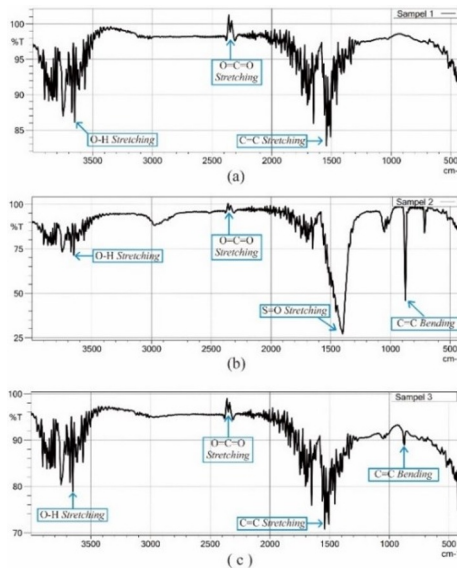
Fig. 5. FTIR testing result (a) Nanocarbon, (b) Nanocatalyst, and (c) A mixture of 20% nanocatalyst and 80% nanocarbon.

Sample (a) is carbon nano. Then in sample (b) is a nanocatalyst. In comparison, sample (c) is a mixed carburizing media from the most optimal variation value. Graphically seen in Figure 3.4, the test results have a similar spectrum between the three. The graph formed in valleys and peaks due to infrared energy that can be absorbed and reflected in each test sample. From the difference in peaks and valleys captured, there is no significant difference, indicating no drastic change in functional groups. In samples (a) and (c), there is only a slight difference in the wavenumber and peak shape; even the per cent transmittance value is almost similar. Both samples have almost the same absorption. The absorption of the O-H stretching group is a type of alcohol compound at 3700-3584 cm-1, at 2400-2349 cm-1 type of carbon dioxide compound with O=C=O stretching, and in 1648-1638 cm-1 region, which shows an alkene compound with C=C stretching vibration.

Sample two of the three media samples tested has a different peak at a wavenumber of 800-900 cm. In sample (a), there is no such peak at that wavenumber, and sample three shows a new peak. An absorption wavenumber of 895-885 cm-1 shows a C=C bending group, a vinylidene-type alkene compound. This type of compound is volatile and flammable. This compound is likely formed from the addition of pearl oyster shell nanocatalyst.

Regarding the difference in clusters that occur, it provides vibrational energy to encourage carbon atoms to diffuse into the core of the specimen. This energy is also directly proportional to the resulting hardness number. The addition of nanocatalysts also gives a higher surface hardness number, better carbon diffusion into carbon steel and visible from the microstructure with a marked increase in the hardness value [16,17].

4 Conclusions

Three conclusions can be drawn through the discussion that has been presented, referring back to the problem formulation written in the introduction. First, pack carburizing treatment can increase surface hardness due to carbon diffusion, with nanocarbon carburizing media from coconut shells. The highest hardness of 255 HV equals an increase of 91.3% with untreated specimens.

Secondly, the addition of nanocatalysts from pearl oyster shells also affects the pack carburizing process, by the function of the catalyst, namely as an additional energy (energizer) to accelerate the carbon diffusion process. The effects can be seen when the carburizing media, with a mixture of 20% nanocatalyst variations, can produce the most optimum hardness number compared to variations without the addition of nanocatalyst. The increase was 10.7% by producing a hardness value of 255 HV, while without nanocatalyst only amounted to 230 HV.

Third, FTIR testing was carried out on the three samples of carburizing media variations. The data is similar; this can be seen through the comparison between samples one and three, which produces a difference in the graph. The graph is found at the absorption value of 895 – 885 cm-1, which shows the C = C bending group. The group is a vinylidene-type alkene compound. In sample one, there is no visible cluster. Then in sample two, it is obvious.

Moreover, the cluster begins to appear in sample three, which is a mixture. From the cluster that began to be seen, it is likely to come from the additional nanocatalyst added to sample two, with vinylidene-type alkene compounds, which are volatile and flammable. The effect of the new cluster is also in line with the hardness testing through nano-catalyzed samples, showing higher hardness values when compared to specimens treated without adding a nanocatalyst.

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