The Effect of Thermo Reactive Diffusion (TRD) Processing Time with Ferrochromium Powder on Carbide Layer Characteristics on SUJ 2 Tool Steel Substrate

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Abstract. In this study, the formation of chromium carbide layer on SUJ 2 tool steel substrate as a surface treatment by thermo reactive diffusion process with pack cementation method was observed. The powder used are Al2O3, NH4Cl, and FeCr as carbide forming elements with the composition of 37%, 3%, 60% for each. TRD process performed in rotating vacuum furnace for 4, 6, and 8 hours on 980°C. The results show time variation effects on the carbide layer. Thickenss carbide layer on SUJ2 after TRD process observed by Optical Microscope. The morphology of carbide layer observed with SEM shows a smooth and dense layer with almost no porosity formed. Cr7C3 and Cr23C6 found on the layer by XRD and hardness value obtained using Vickers microhardness testing for each samples are 1738.62, 1738.72, and 1739.64 HV. The wear rates are inversely proportional with the hardness value where the values are 0.000698, 0.000658, and 0.000627 mm3/m.

Keywords: Thermo Reactive Diffusion, Chromium Carbide, Pack Cementation

1. Introduction

Thermo Reactive Diffusion is a method to form a very hard carbide, nitride, or carbonitride layer which has an excellent wear resistance on a carbon steel substrate [1]. From this process, hard ceramic coating’s expected to formed, which can be used to increase the service life of engine components, cutting tools, and forming tools, usually consist of carbide or carbonitride [2] with a layer that has a better adhesion properties [3]. TRD coating that has been done, mostly using Vanadium as Carbide Forming Elements to produce VC (Vanadium Carbide) coating with a great hardness surface. But, its resistance from oxidation in high temperature still below Chromium [1].

Carbon diffusion process takes place in two stages [4], carbons from the inside of metal move to the surface by heating process so that the surface has relatively higher concentration of carbon and CFE inside the medium reacts with carbon in the surface to form a carbide layer. Kinetic growth of carbide layer itself can be explained by equation below

\[ l^2 = K t = K_0 \exp \left(-\frac{Q_{TRD}}{RT}\right) t \]  

Where \( l \) is thickness (cm), \( t \) is time (s), \( K \) is growth rate constant (J/mol), \( T \) is Temperature (K), and \( R \) is gas constant (8.31415 J/mol K). In this experiment, the effect of different processing time with TRD method at 980°C in 4, 6, and 8 hours towards carbide layer characteristics will be studied. Processing time variable is used to determine the most optimum one in this process.
2. Experimental and Method
Cylinder shaped SUJ 2 steel with diameter 1 cm is cleaned with barrel polishing process. SUJ 2 steel chemical composition can be seen on Table 1. Cylinder shaped SUJ 2 that has been cleaned weighed with pin and mixed with Al₂O₃, NH₄Cl, and FeCr powder by comparison 1:1 for sample : powder, with powder composition on Table 2. Sample and powder are mixed inside the pot and installed into the furnace, vacuum process using Argon gas with 1.5 bar pressure. Vacuum process carried out until -92 KPa reached. Pre-heating process takes place at 400 dan 800°C for 5 minutes each, followed by TRD process for 4, 6, and 8 hours and cooled by furnace cooling process. Sample will be characterized using Optical Microscope (OM) to find out the homogenity of carbide layer that can be seen from the thickness value (measured by infinite analyzer), SEM-EDS to know the morphology and elements distribution of carbide layer, XRD to estimate compounds formed on the surface, wear test to determine wear resistance after TRD treatment, and hardness measurement using Micro Vickers.

| Table 1. Chemical Composition of SUJ 2 Steel. |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Fe    | C     | Si    | Mn    | P     | S     | Ni    | Cr    | Mo    | Ti    | Cu    | Al    | V     |
| Bal   | 1.03  | 0.24  | 0.28  | 0.013 | 0.006 | 1.68  | 0.004 | 0.007 | 0.05  | 0.1   | 0.006 |

| Table 2. Powder Coating Composition. |
|-----------------|---|
| Al₂O₃            | 37%   |
|                  | 300 gram x 37% = 111 gram |
| NH₄Cl            | 3%   |
|                  | 300 gram x 3% = 9 gram |
| FeCr             | 60%  |
|                  | 300 gram x 60% = 180 gram |

3. Result and Discussion

3.1 The Effect of Processing Time Variable On Layer Thickness
From TRD process using Chromium as carbide forming elements, the chromium carbide layer obtained has a compact and smooth surface with low porosity which can be seen on Figure 1. The layer obtained has uniform thickness on sample (a), (b) and (c). The boundary layer and surface clearly seen without any additional layer between them which has a similarity with F.E Castillejo’s experiment [7] so that we can say that there is no interdiffusion layer formed. It also can be proved from the linescan data that shows no additional elements found on carbide layer and substrate as seen on the graph in Figure 2 and 3. The longer the time process, the thicker the layer formed [8] thickness value from 4, 6, and 8 hours time process increases in sequence. For 4 hours processing time, thickness value obtained is 13μm, for 6 hours processing time, the thickness value is 13.7μm, and for 8 hours processing time, the thickness values is 17.2μm.
Figure 1. (a) Carbide Layer $t = 4$ hrs, (b) Carbide Layer $t = 6$ hrs, (c) Carbide Layer $t = 8$ hrs.

In Figure 2 and 3 can be seen the result of EDS linescan characterization which shows elements distribution throughout the carbide layer and surface of the substrate.

Figure 2. Linescan characterization of Carbide Layer (a) $t = 4$ hrs, (b) $t = 6$ hrs, (c) $t = 8$ hrs.
From the linescan graph above, can be seen the tendency that occurs to all samples are the same. Cr content is decreasing from layer to substrate and so the carbon content, even not really significant because the carbon on the surface already bond with carbide forming elements on the layer. It’s proven that the diffusion direction moves from the middle of the substrate to the surface, when the heating process happens, the carbon will gather in the surface area of the substrate. The carbon gathered then reacts with carbide forming elements powder and forming Chromium Carbide layer.

3.2 Analysis of The Compound Formed On The Layer

Figure 3. CPS VS Distance Graph (a) t = 4 hrs, (b) t = 6 hrs, (c) t = 8 hrs.

Figure 4. XRD Characteristics Graph.
From XRD characterization that already converted with X’pert Highscore Plus software, the peaks as seen on Figure 4 was obtained. From the graph above, the compounds identified as chromium carbide found in the form of Cr$_{23}$C$_6$ and Cr$_7$C$_3$ that also found in F. E. Castillejo’s experiment [7], which performs Thermo Reactive Diffusion process using AISI D2 tool steel as the substrate, so it can be proved that the carbide layer is formed in this experiment.

3.3 The Effect of Processing Time On Thickness Value and Homogenity of Layer Formed

Based on the experiment by Fernandes [8], it’s stated that the longer the processing time, the thicker the carbide layer formed. It is the result from the diffusion process that runs longer. From the measurement process, layer thickness obtained from 4, 6, and 8 hours processing times are 13, 13.8, 17.6 µm. Thickness value between 4 and 6 hours processing time are not that different, meanwhile for 8 hours processing time has the thickest carbide layer with a significant difference as can be seen in Figure 5. It supports the theory explained before that the longer the process, the carbide layer formed will also higher. The significant difference between thickness value of 8 hours processing time with the others might be because it is the most optimum processing time in this process.

Thickness increases alongside with increasing processing time in accordance with equation $d^2 = Kt$ [3] where $d$ is layer thickness, $K$ is diffusional coefficient, and $t$ is processing time. The equation shows the longer the processing time, the thicker the layer. Thickness value variation can be made as a layer homogeneity reference. Based on the experiment by M. Bayu [9], coating process using powder mixture of FeCr and FeV with TRD, thickness increases alongside with increasing processing time. The difference of thickness value obtained can be influenced by powder composition used in the TRD process. Where M. Bayu using powder contains Vanadium which affinity towards carbon is higher than
Chromium so that the layer formed also thicker. From the collected data, carbide layer obtained is quite homogeneous and can be proved by thickness measurement result on 3 points for 4 different areas of sample’s surface that shows insignificant difference for each parameters. Layer homogeneity can also be supported by morphology condition that shows compact surface with low porosity.

Figure 7. (a) Homogenity Measurement (b) Homogenity Measurement Result.

Figure 7 shows result from measurement process on layer thickness using OM and Infinite Analyzer Software to determine the value for each points in different areas. Figure 7 shows thickness value distribution taken from 4 different areas for every sample where each area measured three times on three different points, generates an average thickness value. For each parameter, layer thickness obtained have relatively similar values.

3.4 The Effect of Processing Time On Hardness Value
Coating process with TRD method applied for each sample takes place at 980°C with processing time parameters are 4, 6, and 8 hours. Figure 8 shows that hardness values for 4, 6, and 8 hours processing time are 1738.62, 1738.72, and 1739.64 HV. It can be seen that hardness value didn't change significantly for different amount of processing time, it shows that holding time is not affect significantly towards hardness value, the same as found on F.S. Chen’s experiment [1]. It is also show that different processing time will not affect any change in carbide compound forming so that the hardness value will also not be affected.

Figure 8. Hardness Value vs Holding Time.
Based on XRD characterization, the compounds found in the form of Cr$_2$C$_6$ and Cr$_7$C$_3$, from G. Cios’s experiment, it is said that chromium carbide can be classified based on its hardness value. Cr$_2$C$_6$ has hardness value around 976-1750 HV and for Cr$_7$C$_3$ the hardness value is 1336-2200 HV [10] so there is a resemblance between the theory and what we found from this experiment because the data obtained from this experiment is still in the same range with the theory.

3.5 The Effect of Processing Time Towards Wear Resistance

Wear test was done using Ogoshi testing method with 12 kg load, 400 m sliding distance, and 2.38 m/s velocity. From the data obtained, the wear rate tendency is reduced alongside with the increasing of processing time. Figure 9 shows that for 4, 6, and 8 hours processing time, the wear rate values are 0.000698, 0.000658, dan 0.000627 mm$^3$/m. Wear rate value has no significant difference, it can be explained from the insignificant hardness values for each different sample that also affects the wear rate values.

4. Conclusion

Hardness values obtained for 4, 6, and 8 hours processing time are 1738.62, 1738.72, 1739.64 HV that occupies minimum hardness specification for silent chain pin which is 1700 HV and wear rate values are 0.000698, 0.000658, 0.000627 mm$^3$/m. Increasing processing time for Thermo Reactive Diffusion resulting thickness value of 13 $\mu$m, 13.8 $\mu$m, dan 17 $\mu$m. Carbide layer thickness increases due to diffusion process that going on continuously along with the increasing of processing time that can be explained by $d^2 = Kt$ equation. Carbide layer from Thermo Reactive Diffusion process using FeCr powder as carbide forming elements produce Chromium Carbide coating with smooth and uniform surface and carbide compounds on the layer found in the form of Cr$_2$C$_6$ and Cr$_7$C$_3$. For every processing time variable, layer homogeneity measured are uniform. The longer the processing time, the better the homogeneity. The optimum processing time for TRD in this process is 8 hours.

Acknowledgement

Authors would like to thank to Ministry of Higher Education of Republic of Indonesia and Directorate Research and Public Services of University of Indonesia for financial support and project administration respectively to conduct this research under PITTA Project for 2018 fiscal. The Author also would like to thank PT Federal Superior Chain for their support on this research. The Assistance of PT Federal Superior Chain for Thermo Reactive Deposition process and Equipment is gratefully acknowledged.
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