Effect of FeV Residual Powders as an Innovation of Thermo Reactive Deposition Process (TRD) with Material Balance Method to Carbide Surface Characteristics on SUJ2 Tool Steel

Reza Fawazul¹, Myrna Ariati Mochtar²*
¹,² Department of Metallurgical and Materials Engineering, Faculty of Engineering, Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia

myrna@metal.ui.ac.id

Abstract. Thermal Reactive Deposition (TRD) using pack cementation method with vanadium as carbide former has been examined to form the carbide layer on SUJ2 tool steel. In this study, effect of addition recycled FeV powder to new FeV powder to the product quality. Calculation analysis resulted 4 variations of FeV powder ratio to be studied i.e. 100% new FeV powder; 100% residual FeV powder; new powder FeV : residual FeV powder 50%:50%; New FeV powder : residual FeV powder 25%:75%. Electron microscope (SEM) and optical microscope (OM) analysis showed that the carbide layer formed in each sample had the same relative layer thickness of about 18μ. X-ray diffraction (XRD) characterized showing that there were a vanadium carbide compound in the formed layer. Hardness test and wear test resulted a relatively similar hardness value of about 1800 HV and 3x10−5 mm²/m. It can be concluded that the use of residual FeV powder to the new FeV powder can be applied because the test results with various ratios that have been done have relatively similar results and meet the hardness application specification of 1700 HV.

Keywords: Thermal Reactive Deposition, vanadium carbide, SUJ2 steel, residual FeV powder, FeV powder ratio

1. Introduction
Thermo-reactive Deposition (TRD) is the process of depositing carbide-forming elements on carbon-containing surface. This layer have high hardness, good wear resistance, low friction coefficient, oxidation resistance and good corrosion resistance [1-3]. When compared to CVD and PVD, this TRD process has the advantage of not requiring high space to run the process, so that equipment is simpler and reduces production costs [4]. One of the TRD methods is pack cementation which is done by integrating carbide, substrate, Al₂O₃, and NH₄Cl forming powder into furnace with temperature between 950°C until 1100°C. Catalysts fill with carbide-forming powder to produce a carbide layer which will diffuse into the substrate and help impact to get even results. After the process is carried out in a certain period, the substrate is cooled. This process will produce layers with a very high bond between the diffusion layer and the substrate [5].
The vanadizing process aims to deposit vanadium to the material substrate. During the heating process, vanadium atoms diffuse into the surface of the material/substrate. Counter Diffusion of carbon in the material/substrate which will be fundamentally used for the material/substrate and the shape of vanadium carbide as a result of the interaction of carbon to the vanadium layer. From the vanadium carbide for the solid surface layer of vanadium carbide, the vanadium carbide layer formed will have a good performance and does not accentuate the shaft in its layer [6]. Vanadium carbide can achieve hardness of up to 3000 HV and has oxidation resistance at high temperatures (up to 750°C). The reaction is in Equations 1 to 4 [3,7]:

\[ \text{NH}_4\text{Cl}(s) \rightarrow \text{NH}_3(g) + \text{HCl}(g) \]  
\[ 2\text{NH}_3(g) \rightarrow \text{N}_2(g) + 3\text{H}_2(g) \]  
\[ 2\text{HCl}(g) + \text{V}(s) \rightarrow \text{VCl}_2(g) + \text{H}_2(g) \]  
\[ \text{VCl}_2(g) + \text{C}(s) \rightarrow \text{VC}(s) + \text{Cl}_2(g) \]

But during its application, generally there is always residual powder after the surface hardening process ends. This residual powder is no longer used in the process. This research will examine the effect of FeV residual powder (recycled FeV powder) from TRD results on SUJ2 tool steel into FeV new powder in TRD process, on the coating thickness, hardness, microstructure, and elements distribution in carbide layer formed. So that the utilization of residual FeV powder is expected to save production costs from the motor vehicle industry.

2. Experimental Method

This research uses SUJ2 steel samples which have been cleaned and mashed, ferrovanadium powder (FeV), Alumina powder (Al\(_2\)O\(_3\)), and NH\(_4\)Cl powder. Before the research was carried out, it was necessary to do a normal vanadizing process which aims to obtain FeV residual powder which will be analyzed for the composition of the elements between the new powder FeV (powder before the process) and the remaining powder FeV (powder obtained after the process is carried out). This analysis was carried out by XRF analysis which aims to determine the calculation approach to be carried out to add a number of new powder FeV to the residual FeV powder.

After testing is complete and the product is obtained, some characterization of the material will be carried out to observe the carbide layer formed. Characterization carried out is microstructure observation with Optical Microscope (OM), layer morphology observation and element distribution by Scanning Electron Microscope - Energy Dispersive Spectroscopy (SEM-EDS), observation of compound composition with X-Ray Diffraction (XRD), layer hardness test and wear resistance layer.

3. Results and Discussion

| Table 1. XRF Analysis Result of New FeV Powder, in wt% |
|---------------------------------------------------------|
| Element | Mg | Al | V | Fe | Si | P | Ni | Mo |
| %       |    |    |   |    |    |   |    |    |
| 18,75   | 29,43 | 44,69 | 5,71 | 0,97 | 0,23 | 0,035 | 0,012 |

| Table 2. XRF Analysis Result of Residual FeV Powder, in wt% |
|----------------------------------------------------------|
| Element | Mg | Al | V | Fe | Si | P | Ni | Mo |
| %       |    |    |   |    |    |   |    |    |
| 5,78    | 32,27 | 49,49 | 11,23 | 1,01 | 0,12 | 0,08 | 0,02 |

Calculation analysis is performed to determine the percentage difference of the most important elements in powders such as vanadium before and after the TRD process. So we can find out how much new powder FeV needs to add to the residual FeV powder. Table 1 and Table 2 are the results of XRF analysis which shows the levels of elements in the new powder FeV and the recycled powder of FeV in the same series of processes.
For the calculation to be carried out, we want to know how many grams of vanadium are contained in each powder. It is known for the new powder FeV analyzed at XRF that is weighing 10.5376 grams, while for the remaining powder FeV analyzed in XRF weighing 11.2518 grams. Calculations to find out how many grams of vanadium are contained in each powder is done by calculating the usual chemical equilibrium in equation below:

\[ \% \text{ element} = \frac{\text{element grams}}{\text{total grams}} \times 100\% \]  

(5)

So it can be obtained for:

- **new FeV powder**  \[ \% \text{ element} = \frac{\text{element grams}}{10.5376 \text{ gr}} \times 100\% \]  

(6)

- **residual FeV powder**  \[ \% \text{ element} = \frac{\text{element grams}}{11.2518 \text{ gr}} \times 100\% \]  

(7)

Vanadium are obtained = 4.709 grams

Vanadium are obtained = 5.5685 grams

From these two results, there are 4.709 grams of vanadium in 10.5376 grams of FeV new powder and there are 5.5685 grams of vanadium in 11.2518 grams of residual FeV, it can be concluded that vanadium levels are not reduced because the results obtained from these calculations show the vanadium obtained in the new powders did not show a decrease in residual FeV powder. This can be seen from the distance between the total weight of the two powders, namely 10.5376 grams and 11.2518 grams, and also the distance between the weight of vanadium obtained from the calculation of 4.709 grams and 5.5685 grams having the same range of 0.7 grams.

From the conclusions obtained based on this calculation, a research will be conducted on how the difference in the use of residual FeV powder on SUJ2 steel. Whether its obtained the different results from those using only FeV new powder or have the same results. Also, because it is assumed that the vanadium level does not change, it will also be done mixing new powder and FeV residual powder and will also see whether it will have different results or not.

Since it is assumed that the vanadium content in FeV residual powder is not reduced, it is estimated that the experiments to be carried out will have results that are not much different. The experiment will be carried out with the following variables:

New FeV powder, Residual FeV powder 100%, New FeV powder 50% : residual FeV powder 50%, New FeV powder 25% : residual FeV powder 75%.

3.1 Analysis of the Use Effect Recycled FeV Powder on the Carbide Layer Morphology

The carbide layer morphology resulting from vanadizing process for various variations of FeV powder ratios is shown in Figure 1. The morphology of this carbide layer is obtained from the results of SEM testing. In the results of these tests, it showed that the carbide layer is formed in each variation of the use of FeV powder and with similar relative layer morphology.

In the SEM test results, also obtained the thickness of the layers formed in the observed area. From the results of these tests, obtained results with carbide layer thickness size that is not significantly different. This is consistent with the hypothesis that the use of residual powder will be obtained by products with results that will not be much different from products that use 100% new FeV powder without recycled FeV powder mixture.
3.2 Analysis of the Use Effect Recycled FeV Powder on the Carbide Layer Homogeneity

This analysis is conducted to find out whether there are differences in the thickness of the layers formed from each variable. This analysis is shown in Figure 2, which is a combination of 4 images with different positions taken from the same variable. For 1 picture there will be 3 measurements so that the total for 1 variable will get 12 measurements which will be averaged and compared to other variables whether there is a significant difference in the thickness of the carbide layer formed or not.

Figure 1. Morphology of carbide layers (a) new FeV, (b) 100% Residual FeV, (c) New FeV 50% : Residual FeV 50%, (d) New FeV 25% : Residual FeV 75%, resulting from the TRD process for various variations of FeV powder ratios on SUJ2 tool steel.

Figure 2. The homogeneity of carbide layers resulting from the vanadizing process for various variations of FeV powder ratios in tool steel SUJ2 TRD Process Results.
From the results of these observations obtained the average of each variable is as follows:

Table 3. Average Thickness of each variable.

| Powder                                      | Average Thickness (μm) |
|---------------------------------------------|------------------------|
| New FeV powder                              | 18.0125                |
| Residual FeV 100% powder                    | 17.9283                |
| New FeV powder 50% : Residual FeV powder 50%| 18.2792                |
| New FeV powder 25% : Residual FeV powder 75%| 18.2092                |

From the results of these calculations as shown on the table, it showed the carbide layer formed has an average thickness that is not much different. So the use of FeV residual powder that is done will not have much different results from products that only use FeV powder.

3.3 Element Distribution Analysis

In the SEM (Scanning Electron Microscope) test that has been carried out, there are also EDS (Energy Dispersive Spectroscopy) to determine the distribution of chemical elements in the observed area. This analysis is carried out by drawing a straight line starting from the carbide layer which is formed to the base of the material being tested. This analysis aims to determine the distribution of elements in the carbide layer to the material base of each variable.

In Figure 3, shows the results of linescan SEM-EDS analysis that have been done. The results of the analysis showed that there was no difference in the distribution of elements between products using residual FeV powder with products that only used FeV new powder. From the graphs obtained, the vanadium element found in the layers is very high. This shows that the carbide layer is formed in each variable.
Figure 3. Linescan carbide layer results example from the vanadizing process for various variations of FeV powder (a). The graphics show the EDS result of: new FeV (b), residual FeV 100% (c), new FeV 50% : residual 50% (d), new FeV 25% : residual FeV 75% (e) on Tool Steel SUJ2 TRD Process Results.

3.4 Compound Composition Analysis
Observation of the composition of compounds contained in the sample analysed by XRD (X-Ray Diffraction). Observations obtained from this XRD will then be processed by the XRD application, one of which is X’Pert HighScore Plus. The results of these observations are shown in Figure 4 as follows.

In Figure 4, there are at least 3 peaks which represent the dominant compounds found in Vanadizing’s SUJ2 Steel. When matched with the vanadium XRD database/literature for vanadium compounds, these 3 peaks are vanadium carbide compounds. The detected vanadium carbide compounds are V6C5 and V8C7.

The detected Vanadium Carbide compounds were also found in the study of Aliakbar Ghadi [4] and Bayu Mahardika [8] who also carried out surface hardening with the TRD method and used FeV powder. This shows that the use of FeV residual powder applied in this study can produce carbide layers containing vanadium carbide compounds.
Testing the hardness of the SUJ2 Steel sample from vanadizing is done by Microvickers where the hardness results can be directly available from the measuring instrument. The results of the hardness testing can be seen in Figure 5, belows.

The hardness testing was done on the SUJ2 Steel pin by giving each 1 point on 10 samples for 1 variable. The results of this hardness test obtained the average hardness of each sample variable that was not significantly different.

This test uses the Ogoshi method where the test object obtains the frictional load of the rotating ring. From the width of the abrasive material gap, it can be obtained for the wear rate of each sample are:
### Table 4. Abrasive Width and Wear Rate in SUJ2 Steel Vanadizing Results with Various FeV Powder.

| FeV Samples                                      | Abrasive Width (mm) | Wear Rate (mm³/m)       |
|-------------------------------------------------|---------------------|-------------------------|
| New FeV Powder                                  | 1.3                 | 1.0866 x 10⁻⁵           |
| Residual FeV Powder                             | 1.2                 | 1.4363 x 10⁻⁵           |
| New FeV Powder 50% : Residual FeV Powder 75%    | 1.05                | 5.7252 x 10⁻⁵           |
| New FeV Powder 25% : Residual FeV Powder 75%    | 1.1                 | 6.5826 x 10⁻⁵           |

From the table we could see the wear rate was not significantly different. So it can be concluded that the use of recycled FeV powder has a sample quality that is not so far from the sample that only uses new FeV powder.

### 4. Conclusion

Based on the results of research on the use of residual FeV powder as an innovation of the Thermo Reactive Deposition (TRD) process with the Matierals Balance method on the characteristics of carbide layers in SUJ2 tool steel it can be concluded that the effect of using residual FeV powder with various ratios on new powder FeV results in the quality of carbide coating has a thickness that is relatively the same as the carbide layer produced by products that only use FeV new powder. The calculation approach used to determine the addition of FeV new powder to residual FeV powder is carried out using the usual chemical equilibrium calculation method. The calculation is done after obtaining data on the percentage of vanadium in the new powder FeV and recycled FeV powder. The quality of the products produced by the use of recycled FeV powder with various ratios that have been carried out has relatively similar results with products that only use FeV new powder both from the results of carbide layer morphology, layer homogeneity, hardness, and wear resistance.

### Acknowledgment

This research is fully funded by PITTA 2018 given by 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. And also in terms of research equipment supported by PT FSCM Manufacturing Indonesia.

### References

[1] X.S. Fan, Z.G. Yang, C. Zhang, Y.D. Zhang, “Thermo-reactive deposition processed vanadium carbide coating: growth kinetics model and diffusion mechanism”, *Surface & Coating Technology*, volume 208, 2012, pp 80-86. doi: 10.1016/j.surfcoat.2012.08.010

[2] T. Arai, “Thermoreactive Deposition/Diffusion Process for Surface Hardening Steels,” *ASM Handbook Vol 04, Heat Treating*, ASM International, 1991, pp. 1000-1003.

[3] N. Tecnolog and D.Fechea, “Vanadium carbide coatings produced on gray cast iron using the thermo-reactive deposition / diffusion technique,” *Ingeniera Mecanica Tecnologia Y Desarrollo*, volume 5, 2015, pp. 333-338.

[4] A. Ghadi, M. Sohtanieh, H. Saghaian, and Z. G. Yang, “Investigation of Chromium and Vanadium Carbide Composite Coatings on CK45 Steel by Thermal Reactive Diffusion” *Surface and Coating Technology*, volume 289, 2016, pp 1-10.

[5] F. Fazlalipour, M.Aghair-Khafri, “Vanadium carbide coatings on die steel deposited by the thermo-reactive diffusion technique”, *Journal of Physics and Chemistry of Solids*, volume 69, 2008, pp 2465-2470. doi: 10.1016/j.jpcs.2008.04.040

[6] A. Borisova, Y. Borisov, E. Shavlovsky, I. Mits, L. Castermans and R. Jongbloed, “Vanadium Carbide Coatings : Deposition Process and Properties,” *Reutte, volume 2*, 2001, pp 452-468.
[7] C. Oliveira, R. Riofano and L. Casteletti, “Formation of carbide layers on AISI H13 and D2 steels by treatment in molten borax containing dissolved both Fe–Nb and Fe–Ti powders,” *Material Letters, volume 59*, 2005, pp. 1719-1722. doi: 10.1016/j.matlet.2005.01.052

[8] M. A. Mochtar, W. N. Putra, B. Mahardika, “Optimizing the dual elemental thermal reactive deposition time in carbide layer formation on SUJ2 tool steel,” *AIP Conference Proceedings*, 2018, pp 1-9. doi: 10.1063/1.5038294