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Study of temperature effect on carbide layer formation behaviour of dual elements thermal reactive deposition on SUJ2 steel substrate

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Abstract. In this research, the formation of carbide layer coating on SUJ2 steel by pack Thermal Reactive Deposition method was studied. Mixture of 35/65 weight percent of ferrochromium/ ferrovanadium (FeCr/FeV) powder was applied as coating elements. The process was carried out at temperatures of 900, 950, and 1000 °C for 6 hours for each temperature. The effects of temperature on layer thickness, microstructures, homogeneity, hardness, and wear resistance were analyzed. The result showed that the higher the temperature, the thicker the layer formed on substrate surface. The higher percentage of vanadium in the coating layer compared to chromium found by EDS Linescan results indicate that vanadium has higher affinity to carbon than chromium. This result also means the possibility of vanadium carbide formation will be higher than chromium carbides, due to the lower Gibbs energy for vanadium carbide formation. XRD results showed that the layer formed in this process consists of vanadium carbide (V8C7 and V6C5), chromium carbide (Cr23C6 and Cr7C3), and complex carbides. The average micro hardness and wear rate of all coatings with three different temperature variations were 2100 HV, and 3 x 10^{-4} mm^3/m respectively. This hardness was close to FeV hardness as single carbide former at approximately 2400 HV.

1. Introduction

The production of thin and hard carbide layer on steel is a widely used treatment to enhance the lifetime of tools, dies, and other mechanical parts. Nowadays, there are three common ways to produce hard carbide coating namely chemical vapor deposition (CVD), physical vapor deposition (PVD), and thermal reactive deposition (TRD) [1]. CVD and PVD have some drawbacks such as high investment cost, and using high vacuum or higly controlled atmosphere [2]. Compared to those process, TRD process has much lower investment cost because it operates at atmospheric pressure and does not need complex equipment.

TRD process can be applied in three different methods i.e. molten salt bath [3, 4], fluidized bed [1, 5], and pack cementation [6, 7]. In these process, vanadium, niobium, tantalum, chromium, molybdenum, or tungsten were used as carbide or nitride forming element. The carbon or nitrogen from steel substrate will diffuse and react with the carbide and nitride forming element, creating a dense deposit, and metallugically bonded carbide or nitride coating [8].

Vanadium and chromium are very frequently used as carbide former for TRD process. Comparing these two elements as carbide forming layers, vanadium carbide has excellent adhesion properties to the substrate, high hardness, and good wear resistance [9-13]. Meanwhile, chromium carbide provides layer which has a good resistant against corrosion and oxidation. Furthermore, chromium carbide former (such as ferrochromium) cost less than vanadium carbide former (such as ferrovanadium) [14]. Using the mixture between FeV and FeCr would combine the advantages of each elements, and simultaneously reduce the production cost. Therefore, the objective of this study is to produce and observe the effect of temperature on mixed vanadium and chromium carbide layer on steel subsrate by pack cementation method. Ferrochromium and ferrovanadium powder were used as carbide formers to produce mixed vanadium and chromium carbide layer on SUJ2 steel.

2. Experimental method

The substrate used in this study was SUJ2 bearing steel. It was a cylindrically-shaped bearing, 2.51 mm in diameter and 6.07 mm in height. Its chemical composition was shown in Table 1. All samples were cleaned by washing with KC99 to produce surface roughness at 0.15 µm. The chemical composition of ferrochromium and ferrovanadium powder were shown in Table 2.

Table 1. Chemical composition of SUJ2 Steel (weight %).

Fe	C	Si	Mn	Ni	Cr
Balance	1.03	0.24	0.28	0.06	1.68

The TRD process performed by the pack cementation method done in this research was using a powder mixture consisting of 195 g of ferrovanadium, 105 g of ferrochromium, 15 g of ammonium chloride, and 185 g of alumina. This powder mixture was then mixed with SUJ2 bearing steel as substrate weighing approximately 500 g. The process was carried out in steel box at 900, 950 and 1000 °C for 6 hours holding duration on each temperature in the furnace, then followed by furnace cooling.

The sample cross section was cut to check the carbide coating and measure its layer thickness. Nital solution (2% HNO_3 dan 98% alcohol) was used to etched the sample, and then observed by optical microscope. Microhardness measurement of the coated layers were carried out with Vickers microhardness tester with 100 gram load and 10 seconds holding time.

Table 2. Chemical composition of : (a) FeCr and (b) FeV (weight%).

(a)

Fe	Cr	C	Si	P
Balance	79%	0.03	1.94	0.024

(b)

Fe	V	C	Si	P	Al
Balance	80	0.15	0.97	0.04	1.2

Wear resistant test were performed using Ogoshi high speed universal wear testing machine with 400 meter sliding distance, and 120 N load at 2.38 m/s sliding speed. The radius and thickness of revolving disk were 14.87 and 3.53 mm respectively.

For phase identification on surface layer, X-ray diffraction (XRD) analysis was conducted for 2θ angles varying from 10° to 100°. The composition of carbide layer was analysed by energy dispersive spectroscopy (EDS) linescan attached within a scanning electron microscope (SEM).

3. Results and discussion

3.1. TRD process temperature effect on the formation of carbide layer

Figure 1 showed the influence of TRD process temperature on carbide layer thickness. It can be seen from the graph that increasing process temperature will produce thicker carbide layer. The mean thickness were 14.5 µm, 24.3 µm, and 30 µm for 900 °C, 950 °C, and 1000 °C respectively.

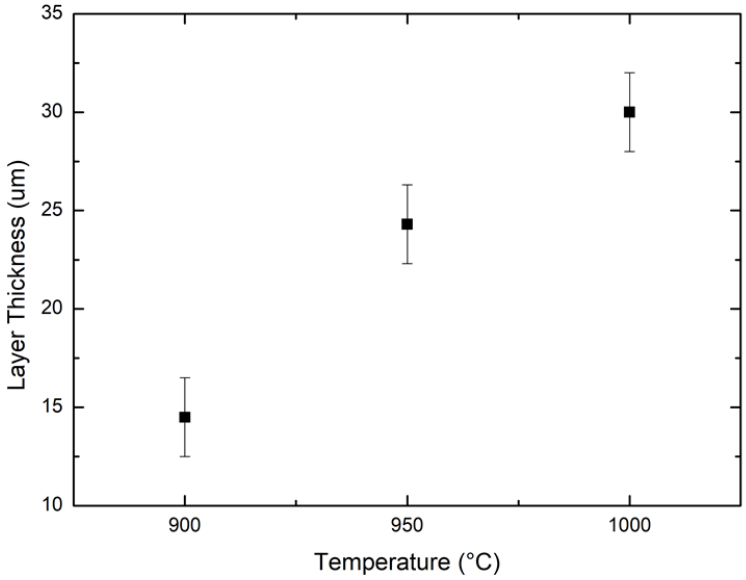

Figure 1. Influence of temperature on thickness.

The relatioship between temperature and layer thickness can be expressed as Arrhenius equation :

$$\frac{d^2}{t} = K = K_0 \exp\left(-\frac{Q}{RT}\right) \quad (1)$$

where d is layer thickness (m), t is time (s), K_0 is pre exponential constant, K is diffusion coefficient (m/s^2), Q is activation energy (joule), and R is the gas constant (8.314 J/mol K). The equation showed that the temperature will affect the diffusion rate of carbon and the carbide former elements [1, 3], whereby increasing the temperature will speed up the forming reaction of carbide layer. Consequently, the coating thickness increases with higher TRD process temperature.

3.2. TRD process temperature effect on carbide layer hardness

The effect of temperature on average layer hardness can be seen in Figure 2. It showed that process temperature did not have a significant impact on average layer hardness. The hardness value tend to be stable at 2100 HV with increasing process temperature from 900 to 1000 °C. By holding for 6 hours at elevated temperature, the carbide compositions formed in the layer were the same for all process temperatures, therefore the hardness values were relatively equal. It indicated that process temperature only affect the layer thickness instead of layer hardness.

This hardness was close to FeV hardness as single carbide former at approximately 2400 HV [2, 15]. The average hardness in this study is lower compared to FeV single carbide former because the chromium carbide phases exist in the layer has lower hardness value than vanadium carbide phases.

The process temperature, in the other hand, has siginificant effect on hardness distribution as shown in Figure 3. The distribution data was taken from 20 samples with 5 measurement points in each samples, totalling in 100 hardness value obtained for each temperature variation. It showed that at 900 °C, hardness is almost distributed evently from 1600 HV to 2800 HV. This might be due to the slower rate of diffusion at lower temperature, so that there is no tendency towards certain phases formed on the layer.

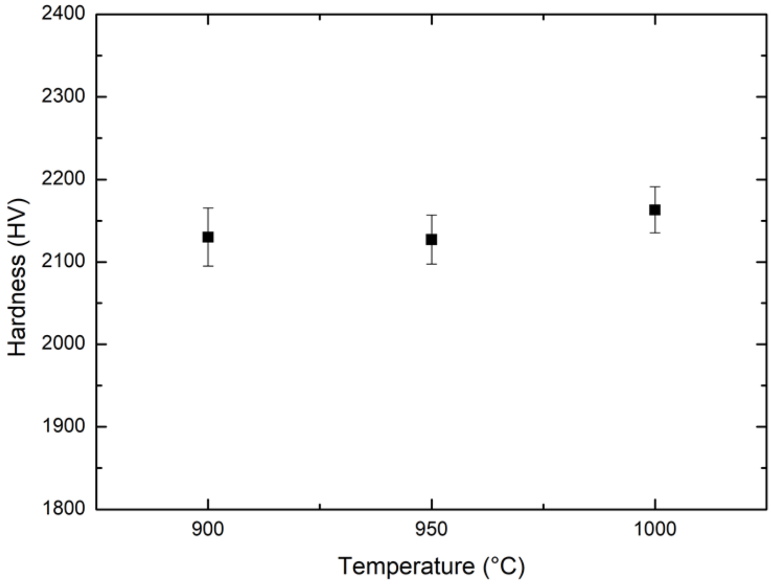

Figure 2. Influence of temperature on layer hardness.

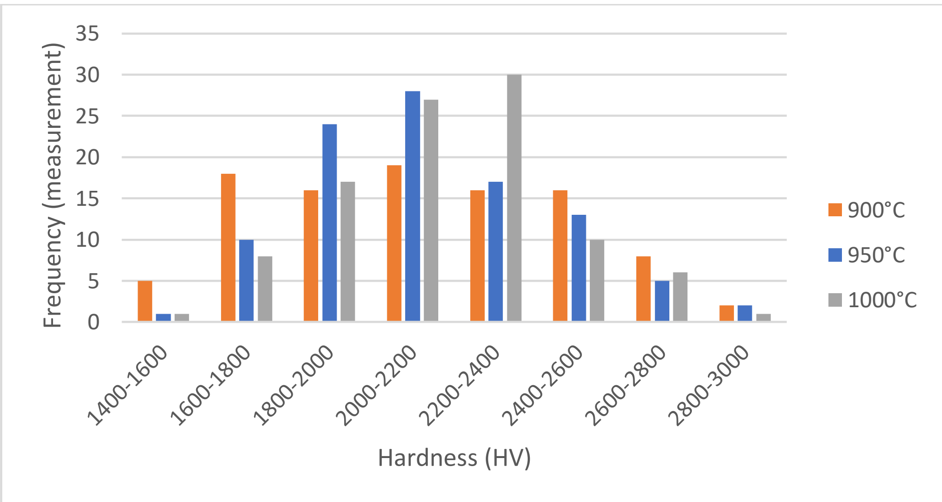

Figure 3. Hardness distribution.

3.3. Characterization of carbide layer

The cross section micrograph of the coated SUJ2 steel which had been processed at 950 °C can be seen in Figure 4. Two distinct regions can be identified on the cross section i.e. vanadium-chromium carbide layer and steel substrate. There is no interdiffusion region observed between steel substrate and carbide layer. This result is similiar with research conducted by X.S Fan [4] and Mattia Biesuz [16], both explaining that the lack of interdiffusion region is due to low solubility product of vanadium and carbon in austenite at TRD temperature.

Different results, however, reported by Aliakbar Ghadi *et al.* when producing mixed vanadium and chromium carbide layer with higher content of chromium in the mixture [10]. The research mentioned ferro-chromium solid solution formed between steel substrate and carbide layer. Therefore, it may be concluded that different result obtained in this research is probably because of low chromium content in the mixture used so that ferro-chromium solid solution was not formed.

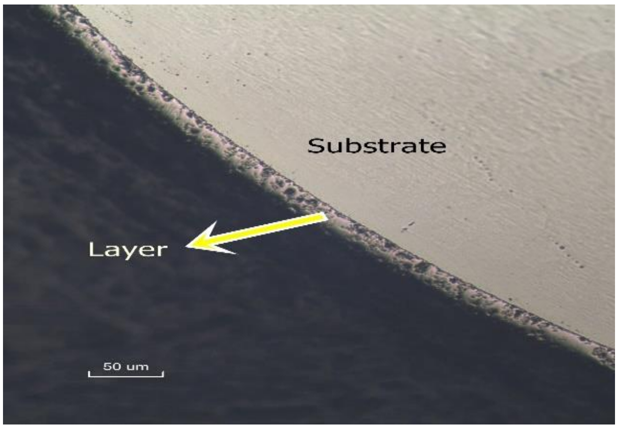

Figure 4. Cross section optical micrograph.

The EDS analysis result proved that interdiffusion ferro-chromium solid solution was not formed between steel substrate and carbide layer. Linescan showed very sharp Fe concentraton profile between substrate and carbide layer as seen in Figure 5. From that figure it can also be observed that vanadium concentration was higher than chromium in the layer. This is because vanadium is stronger carbide former than chromium [17] so that vanadium carbide is more easily formed than chromium carbide.

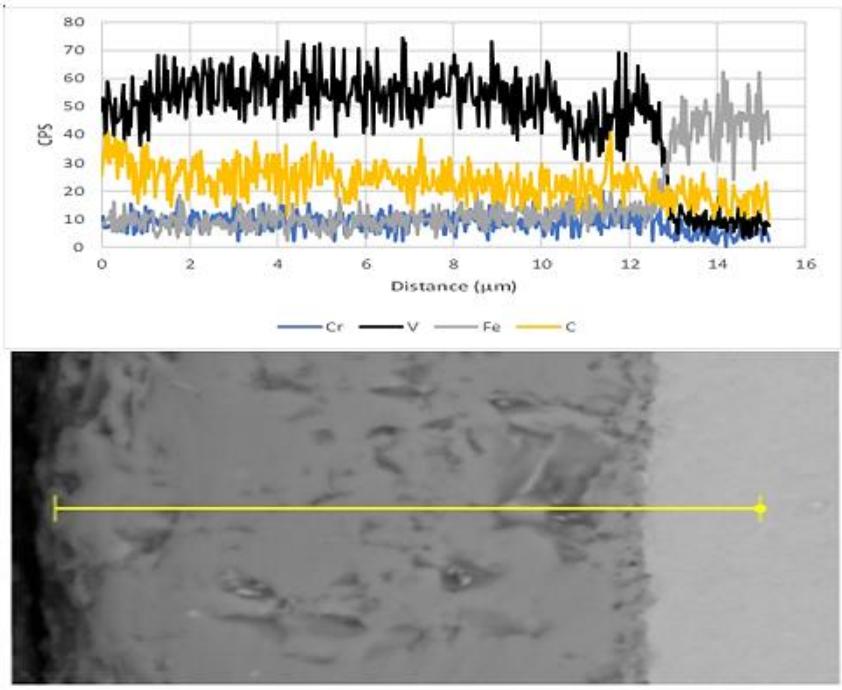

Figure 5. Linescan for TRD process at 900 °C.

Figure 5 also showed that the diffusion of carbide former elements were faster in elevated temperature. During six hours TRD process at 900 °C, the vanadium diffused only 13 μm from the steel surface, while at 1000 °C it could diffuse up to 27 μm. This higher diffusion rate at higher temperature is a well-known thermodynamic phenomenon, expressed by the Arhennious equation in the previous discussion. At elevated temperature, the atoms have more kinetic energy; therefore, they diffuse at a higher rate.

From Figure 6, regions with brighter colour can be observed. From linescan data on that particular region, the concentration of vanadium drop, but the concentration of iron was going up, while concentration of carbon and chromium were still remain the same. Based on this information, we assume that complex carbide which consists of vanadium, chromium and iron was formed in the layer.

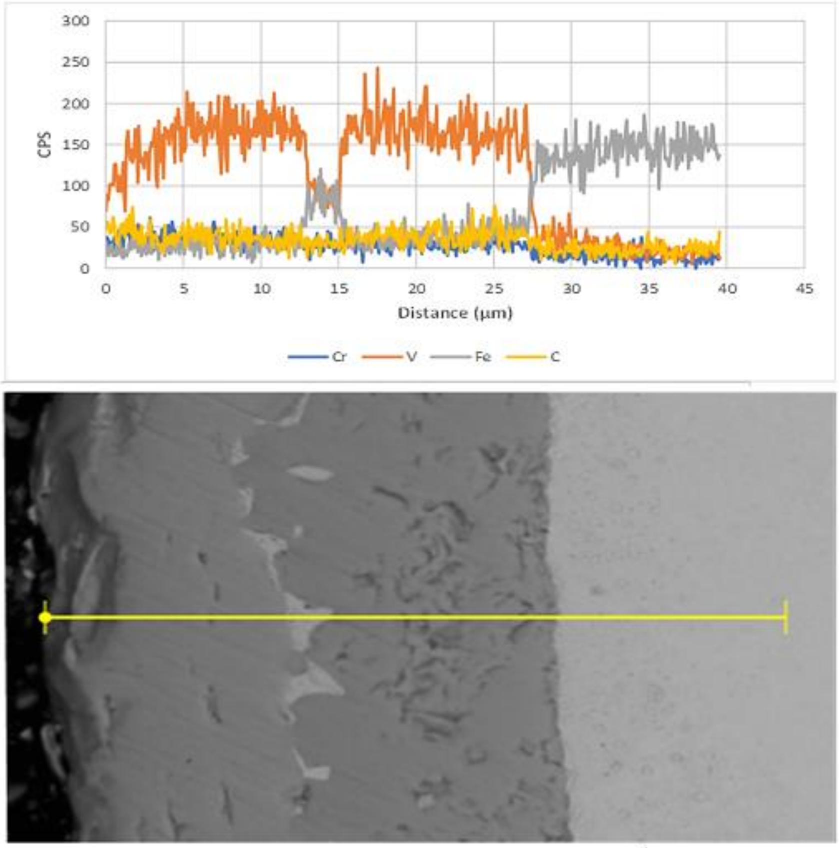

Figure 6. Linescan for TRD process at 1000 °C.

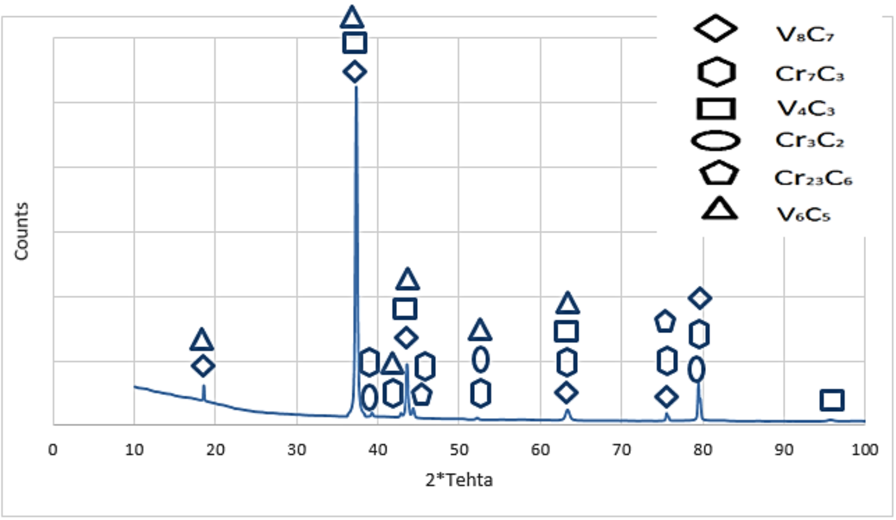

Figure 7. XRD pattern for 900 °C process.

The XRD analysis result of the TRD coating on SUJ2 steel processed at 900 °C is presented in Figure 7. It shows that the layer consists of both vanadium carbide and chromium carbide. Vanadium carbide phases formed in the layer were V_8C_7, V_4C_3 and V_6C_5, while chromium carbide phases formed in the layer were $Cr_{23}C_6$, Cr_3C_2 and Cr_7C_3.

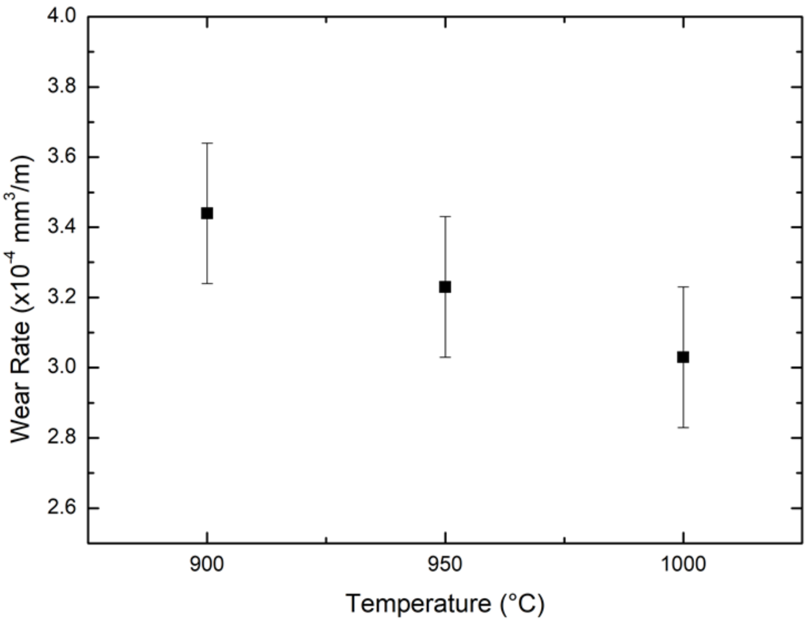

Figure 8. Influence of temperature on wear rate.

3.4. TRD process temperature effect on wear properties

Effect of process temperature on wear rate was shown in Figure 8. It showed that higher process temperature will slightly decrease the wear rate of material from 3.4×10^{-4} mm^3/m at 900 °C to 3.03×10^{-4} mm^3/m at 1000 °C. It may because of higher process temperature, the layer formed become relatively more thicker, denser, and harder. The specific wear rate of this testing was shown in Table 3.

Table 3. Specific wear rate.

Temperature (°C)	Specific Wear Rate ($mm^3/N.M \times 10^{-6}$)
900	2.91
950	2.73
1000	2.55

Research conducted by M.Aghaie Khafrie using FeV as single carbide former, showed a specific wear rate about $6 – 8 \times 10^{-6}$ mm^3/Nm at 140 N load [2]. Compared with mentioned research, the specific wear obtained in this study by using chromium-vanadium as carbide former was somehow have similar values.

4. Conclusion

In this study, a mixed chromium and vanadium carbide coatings layer were successfully formed on SUJ2 steel substrate by pack cementation process. Based on the characterization results, it can be concluded that higher process temperature, the thickness of carbide layer formed is increased. The diffusion occurs faster in higher temperature, where the average thickness obtained at 900, 950 and 1000 °C were 14.5, 24.3 and 30 µm respectively. The resulting thickness was quite homogeneous, showed by only less than 4 µm thickness difference on substrate surface for each process variations. The process temperature, however, has no significant effect on the average coating hardness. The hardness obtained tends to be similar i.e. 2130 HV at 900 °C, 2127 HV at 950 °C and 2163 HV at 1000 °C. This also affects the wear rate which tends to be similar in the three process variations, which is about 3 x 10^{-4} mm^3/m.

EDS Linescan showed higher vanadium content than chromium in the carbide layer, indicating the possibility of higher vanadium carbide formation due to lower Gibbs-forming energy. XRD results showed that the layer formed in this process consists of vanadium carbide (V_8C_7, V_6C_5), chromium carbide ($Cr_{23}C_6$, Cr_7C_3), and complex carbides. The average micro hardness of all coatings were 2100 HV averages. This hardness was close to FeV hardness as single carbide former at approximately 2400 HV.

Finally, mixture of ferrochromium and ferrovanadium powder as carbide former elements can be recommended for Thermo Reactive Deposition process on SUJ2 steel substrate. This mixed carbide former elements could reduce the process cost without sacrificing the mechanical properties, as the hardness value and wear resistance did not decrease significantly compared to the coating using ferrovanadium as single carbide former.

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