The Effect of the Holding Time on the Formation of Niobium-Vanadium Carbide Coating Onto Aisi 420 by Thermo Reactive Diffusion Process

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Abstrak—**The deep drawing process had been widely used in automobile, aerospace, electronics, and allied industries to produce hollow parts. The quality of the deep drawing is determined by the dies properties especially their wear-resistant and hardness. Austenitic stainless steel AISI 420 is one of the material of choice for making these dies. In order to increase the wear resistance of the dies, surface treatment such as thermo-reactive diffusion (TRD) technique can be applied owing to their simplicity, low cost, and environment friendly process. TRD technique able to deposit hard layers of carbide, nitride, or carbonitride In this research, TRD techniques will be employed to AISI 420 with special attention given to the effect of holding time during TRD process to form niobium-vanadium carbide (NbVC) coating. The TRD process is carried out by the powder-pack method in a sealed steel container containing powder mixture of niobium and vanadium as master alloy, alumina (Al2O3) as an inert filler and ammonium chloride (NH4Cl) as an activator. The samples were covered with powder mixture and then heated in the electric resistance furnace for 2, 4, and 6 hours at 1000˚C. The crosssection analysis of the NbVC coating observed under microscopy shows that coating thickness increased with longer holding time with 6.95 μm measured in 6 hours holding time. The high hardness of 1333.2 HV also found in the longest holding time of 6 hours. This high hardness is expected to contribute in the wear resistance characterisitic of AISI 420 dies.**

Keyword—**Deep Drawing Process, Thermo-Reactive Diffusion, Niobium-Vanadium Carbide, AISI 420, Hardness**

Figure 1. Inside the Reaction Pack.

I. INTRODUCTION

VARIOUS methods have been employed to improve the formability of deep drawing process, usually represented by drawability. This was defined as the capacity of the material to assume the designed shape without losing its stability, avoiding fractures, achieve maximum forming force necessary. Sheet metal drawability is usually expressed by its limiting drawing ratio (LDR) which, for an axisymmetric cup, is defined as the ratio of the largest blank diameter that can be formed to the punch diameter. One main factor that affects the formability of the deep drawing process is the frictional force present between the blank and the forming tools. Several methods, such as having harder materials for the forming tools, better surface finish and the use of lubricants have been implemented with much success in reducing friction.

Another method that can be implemented into forming tools is introducing hard coating. Studies have shown that longer tool

Figure 2. Reaction Pack in the Furnace.

Table 1.
Chemical Composition of FeNb and FeV

FeNb		FeV	
P	0.8%	S	0.1%
Al	2.0%	V	75%-82%
C	0.3%	Si	2.0%
Ta	0.2%	P	0.1%
Nb	65%	C	0.25%
Si	3.0%	Al	4.0%
S	0.1 %		

Table 2.
Chemical composition result

Elemen Paduan	Hasil Uji Spectrometer (%wt)	Standar ASTM F899 (%wt)
C	0.35	0.16 (*min*)
Mn	0.59	1.00 (*max*)
P	0.019	0.040 (*max*)
S	0.003	0.030 (*max*)
Si	1.24	1.00 (*max*)
Cr	13.808	12.0-14.0
Mo	0.314	-
N	-	-
Ni	0.31	1.00 (*max*)

Figure 3. After TRD Process.

Figure 4. Thermo Reactive Diffusion (TRD) heat treatment scheme.

life, increased productivity, improved workpiece quality and reduced machining forces are experienced when cutting tools are coated with metal carbides, nitrides and oxides. Nevertheless, there are only limited study available on hard coatings for deep drawing tools even though the coatings had proven to increase the performance of forming and cutting tools.

There are several method available to introduce hard coating onto forming and cutting tools such as chemical vapor deposition (CVD), physical vapor deposition (PVD), lase cladding (LC), in situ synthesis (ISS) and thermo reactive diffusion (TRD). Although CVD, PVD, LC, ISS techniques provide excellent hard coating, these processes are considered expensive and sometimes complex, TRD method is considered as least expensive and simpler as compared to other methods. TRD method is process were a substrate is either immersed into molten borax (salt bath immersion method) or covered with mixture of powder (powder pack method) containing carbide forming element (CFE) such as chrominum, molydenum, vanadium, and niobioum.

Forming and Cutting tools usually using a cold working tool steel such as AISI 420 tool steel is often referred as semi-stainless because it has a high chromium content of 11 to 13 wt. %. This is not high enough to be classified as stainless steel. AISI 420 steel has high wear resistance and high hardness number properties. This is because AISI 420 steel has a high carbon content. In order to improve the properties of wear resistance and achieve higher hardness number, a surface treatment is recommended for AISI 420 steel. Element such as niobium and vanadium are proposed since niobium metal has soft and ductile properties, while vanadium has a higher har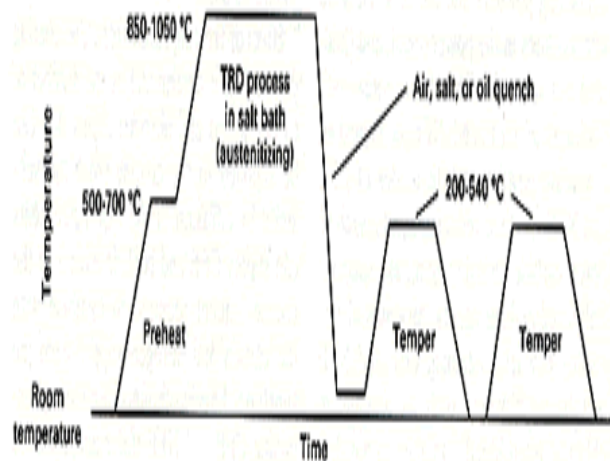dness number when compared to most of the steels and metals. These two elements are widely used as alloying element for cutting tools.

The objectives of this research itsself are to know the effect of the holding time on the thickness of the niobium-vanadium carbide layer resulting from the thermo-reactive diffusion process and to know the hardness of the niobium-vanadium carbide layer affected by holding time of TRD process. this objectives is expected to contribute in the wear resistance characteristic of AISI 420 dies.

Table 3.
Thickness value of TRD porcess

Carbide Coating Thickness Value (μm)		
	TRD 2 hours	TRD 4 hours	TRD 6 hours
Average	5.421138468	6.209490741	6.958912037
Standard Deviation	1.51855539	0.96187597	0.914909377

Table 4.
Micro Vickers Hardness result

Point	Hardness value (HV)			
	Non	TRD 2 hours	TRD 4 hours	TRD 6 hours
average	538.6	976.8	991.1	1333.2
Standard Deviation	26.97818	145.86127	93.66898	98.574056

Figure 5. XRD pattern of holding time analyse at match!3 software.

II. EXPERIMENTAL PROCEDURE

The following is the procedure for conducting research evaluating niobium-vanadium carbide coatings on AISI 420 produces through TRD.

1) Collect sources (book, journal, etc.) as research references.
2) Preparing research tools and materials by considering the methods used, namely thermo-reactive diffusion process.
3) Assembly and welding of the reaction pack according to the specified dimensions.
4) Cut the substrate (AISI 420) using wire cut. The dimension is 3.5 mm for the length and 0.5 for the thickness.
5) The preparation of substrate is performed through metallographic polishing with 120, 240, 320, 400, 600, 800, 1000, and 2000 sandpaper.
6) Fill the reaction pack with powder mixture which consists of 10 wt.% Fe-Nb, 10 wt.% Fe-V, 5 wt.% NH_4Cl, and 75 wt.% alumina. Put the substrate inside them.
7) TRD treatment on test pieces according to the desired holding time 2 hours, 4 hours, and 6 hours with temperature of each holding time is 1000°C, that can be seen in Figure 1.
8) Let the samples are left to cool down in open air, that can be seen in Figure 2.
9) Preparing samples for topographic, elemental and mechanical testing.
10) Testing samples using XRD, hardness test, and microstructure using optical microscope.
11) Analyze test results.
12) Make conclusions from the analysis, that can be seen in Figure 3.

A. Thermo Reactive Diffusion (TRD)

Thermo-reactive Diffusion (TRD) processes are different from general surface hardening processes such as carburizing or nitriding. The TRD process is one of the diffusion hardening me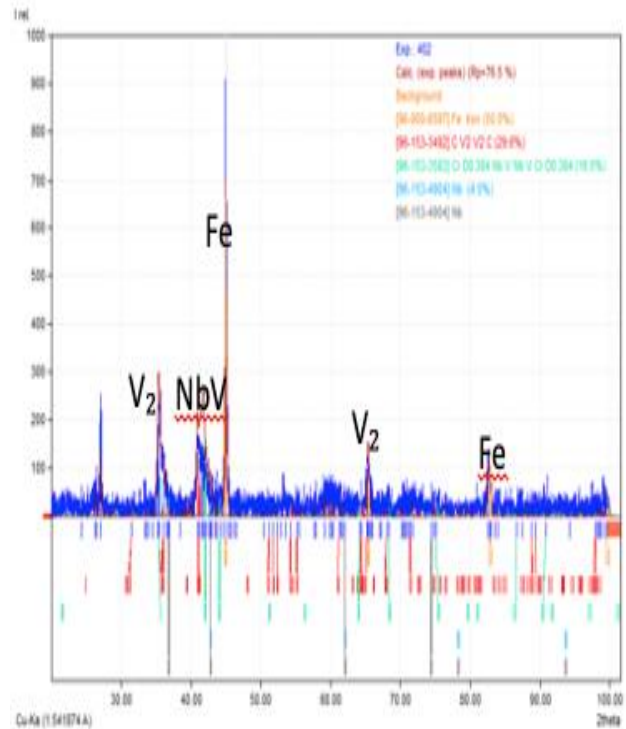thods. In the TRD powder pack process, the component or tool to be coated is placed in a container containing a mixture of alumina powder and Ferro niobium (carbide forming element) and heated at a temperature of 850-1050 C for 2 to 10 hours [1].

For the TRD process as a whole starting from sample preparation can be written as follows.

1) The steel that the TRD process wants to do is the preparation of sandpaper and polish which aims to remove surface oxides that can blocking the niobium from diffusing into the steel.
2) After the sample preparation is carried out the TD process is accompanied by reheating according to Figure 4. This reheating process aims to remove residual stress in steel due to the process fast cooling. This reheating process performed 3 times at 180 oC for 3-5 hours.
3) After washing using water, the sample is done polish before used in applications. This process aims to smooth the surface and aesthetics.

In the TD process, the carbide-forming elements contained in the actve ingredient in alumina pack powder will diffuse into the steel and bind to the carbon in the steel and then form carbides that have high hardness. The formation of carbide in the TRD process takes place through the stages.

1) The carbide forming elements added in powder form are evenly distributed in alumina media.
2) The ammonium chloride activator will help the formation of niobium ions and also cause the carbon on the steel surface to become active.
3) Carbon in steel becomes active and can bind to ions from carbide-forming elements so that it reacts on the steel surface to form a hard layer of carbide.

The carbide layer on the surface thickens due to a continuous reaction between carbon from steel and ions from the activation of carbide-forming elements as the TRD process progresses.

B. Research Variation

In this research, the author will investigate the effect of holding time of TRD process made by powder pack methods onto coating formation and hardness properties.

The variation of the holding time itself means that the holding time that is carried out will be different after the material is entered into the furnace for the heat treatment process. The time that was varied was the time after preheat.

The variation of the holding time that will be carried out in this research is detention for 2 hours, 4 hours, and 6 hours with a temperature of 1000°C. Taking the temperature of 1000°C itself is seen from previous research which shows that the optimum temperature for the TRD process is 1000°C. After determining the temperature and holding time, then next is the mixture powder for the TRD process itself in which consists of NH_4Cl, Al_2O_3, FeNb, and FeV where the presentation taken from previous research shows that the most optimal mixing is 5% NH_4Cl 20% CFE (Fenb Fev) and the rest. is Al_2O_3. Chemical Composition of FeNb and FeV can be seen in Table 1.

C. AISI 420 Martensitic stainless steel as Base Metal

Martensitic Stainless Steel is steel with a chromium content of between 11.5% to 18%, for example, steel of type 420, 440, and 501. This type of steel has magnetic properties, can be carried out cold and hot work easily, satisfactory machinability, especially with low carbon content, has good toughness, shows good corrosion resistance to weather, and some chemicals. This steel can achieve the best corrosion resistance when hardened from the recommended temperature.

D. FeNb and FeV as Master Alloy

Ferroniobium and ferrovanadium are chosen as master alloy bcause they can form hard layers of coating on the surface of AISI 420.

E. Al₂O₃ as Inert Filler

The Al_2O_3 is chosen as inert filler because it has high temperature resistance with a melting point at 2072 C and boiling point at 2977 C. Al_2O_3 also does not react with ionized FeNB and FeV so it does not interfere the TRD process.

F. NH₄Cl as Activator

The activator used in this study is NH_4Cl. The function of the activator itself is to break down FeNb and FeV to bind to the carbon in 420 steel. The effect of activator is considered constant from the start of the treatment to completion.

G. Reaction Pack

The reaction pack used in this study has a function to limit the diffusion reaction, so that it is not disturbed by the external system. The material used for this reaction pack must also have high temperature resistance properties so that it does not interfere with the diffusion process.

III. RESULT AND DISCUSSION

A. Chemical Composition Result

Testing og chemical composition was carried out using the electron spectrometer GVM-514S owned by PT. BARATA INDONESIA. the following **Error! Reference source not found.** which is the result of spectometer test for AISI 420.

From the results of the chemical composition test obtained showed that the chemical composition of stainless steel AISI 420 is better than the ASTM F899 standard due to silicon content of more than 0.24 wt% of the standard which is a maximum of 1.00 and has molybdenum content of 0.314 wt%. This affects the mechanical properties of the material because the levels of silicon and molybdenum present in the material can increase the strength and hardness of AISI 420.

B. X-Ray Diffraction Test

X-ray Diffractionn testing was carried out to determine the chemical composition of treated specimens. Testing uses XRD with 2Θ varying from 10° to 80°. the following is the result of XRD Pattern for the treated specimen.

Data from the results of x-ray testing carried out in the Material and Metalllurgy department, then analyzed using match!3 software to find out what chemical substances were obtained from the test results. From the graph in the Figure shows that the x-ray diffraction test proves that there is a reaction of NbVC and V2C elements. The test results data prove that the coating formation that occurs is the result of the reaction of the elements niobium and vanadium

C. Thickness Test Result

Observation of the coating thickness results from the TRD process was carried out using an Olympus optical microscope with 200x,500x,and 1000x magnification. The specimens prepared for observation are coating area NbVC as a result of TRD with variations at holding time 2 hour, 4 hour, and 6 hour at 1000°C. The following are the results of observations on each specimen.

The XRD results show that there is niobium vanadium carbide in aAisi 420, so it can be concluded that the layer formed around the speciment is a niobium vanadium carbide coating as shown in the Figure 6. The formation of a coating layer around the specimen has a difference in thickness, especially in each variation, therefore to calculate the thickness it will be seen from the average thickness value of several points taken, with a total of 15 points measuring the thickness of each variation as shown in the Table 3.

From the Table 3, it can be seen the thickness value of each variation carried out, namely the variation of holding time at 2 hours 4 hours and 6 hours. It can be seen that the highest thickness is in the holding time of 6 hours with an average value 6.95 µm followed by the holding time of 4 hours with average thickness value 6.20 µm, and finally the holding time of 2 hours with average thickness value 5.42 µm.. From the results above, it can be seen the effect of the length of time holding on the thickness of the coating where with a longer time the coating will be thicker due to the diffusion process that effect the binding time of the carbide forming element that
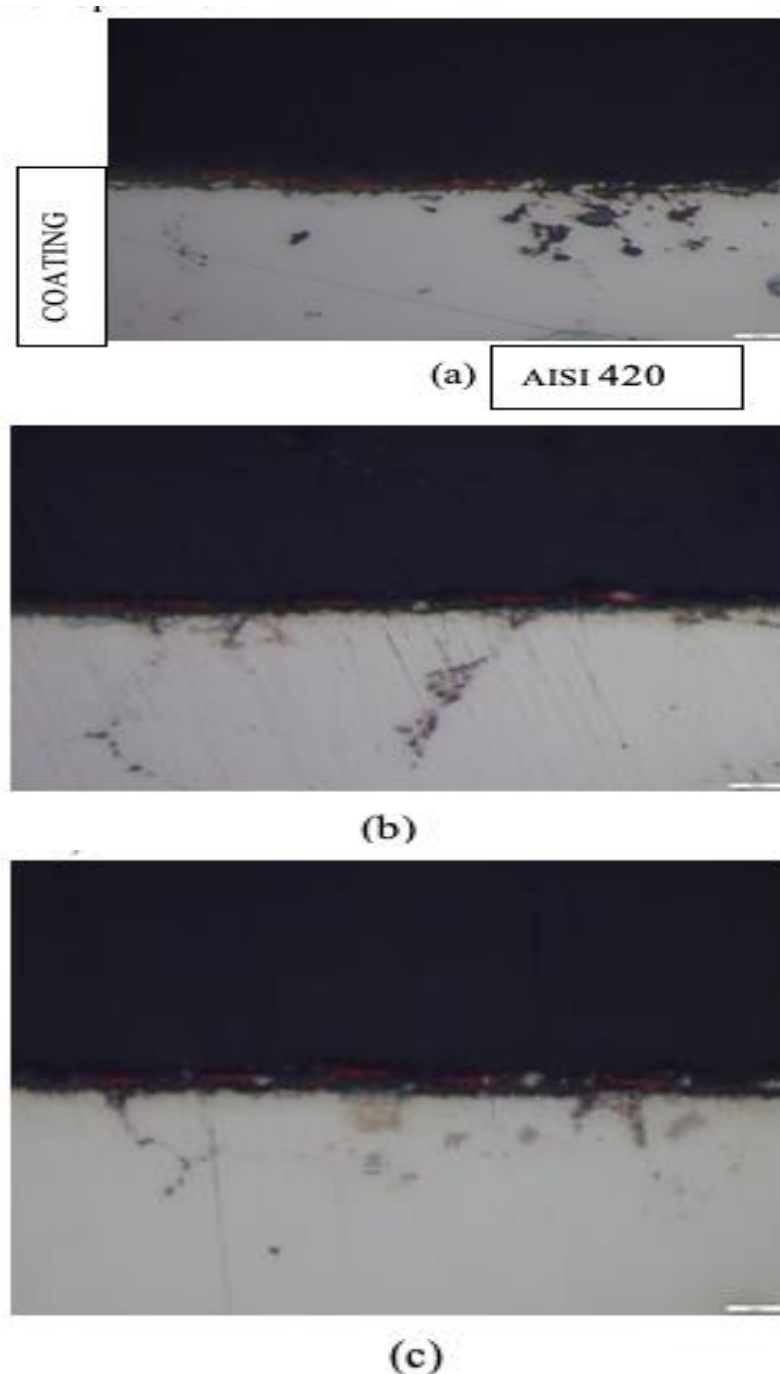
Figure 6. Coating thickness observation with 500x magnification. (a) 6 hours holding time TRD process, (b) 4 hours holding time TRD process, (c) 2 hours holding time TRD process.

occurs in the powder pack when heat treatment is carried out which has a longer time to bind.

D. Hardness Test Result

Micro-Vickers hardness testing was carried out on all specimens with a load of 0.5 HV in the carbide layer formed on the side of the test specimen and in the center of the specimen which did undergo TRD testing 10 times on each specimen, that can be seen in Table 4.

From the data above, it is found that the greatest hardness value in the untreated specimen is 569 HV with an average 528.6 HV. The greatest hardness value obtained in the specimens treated with a hold time of 2 hours is 1203 HV with an average value of 976.8 HV. on specimens with a holding time of 4 hours had the greatest value 1156 HV with an average value 991.1 HV. The greatest hardness value on the specimen with a holding time of 6 was 1487 HV with an average 1333.2 HV.

The untreated specimen has the lowest hardness value compared to the hardness value of the treated specimen. The results above show that the TRD process has the highest value of hardness with a holding time of 6 hours followed by the hardness value of the holding time of 4 hours and finally the hardness value of the holding time of 2 hours. in theory, it

shows in general coating formation processing that, the longer the holding time, the hardest the carbide layer is formed, and in this research, it does show conformity to the theory with the highest hardness values found at the longest holding time and the trend shown there was no decrease in the mean of hardness value of the niobium-vanadium carbide formed. the longer the holding time in the TRD process itsels also effect the homogenity and density fro the carbide layer that is form because it will have the longer time to bind the CFE or niobium and vanadium to the speciment so the homogenity and density will be higher at the 6 hours than at 4 hours or 2 hours, therefore the hardness value will be higher at the longer time.

The difference in hardness values at each point is influenced by the presence of a depleted zone or a carbon-poor area at the indentation point taken. The amount of powder mixture also affects the precense of the depleted zone or a carbon-poor area obtained, the percentage of powder mixture used in this research is 10% nb 10% v 5% NH_4Cl and 75% Al_2O_3 with a content of 222 grams of Al_2O_3, 29.6266 grams of niobium, 29.6266 of vanadium, and 14.813 of NH_4Cl with the grade as stated, with more of the defleted zone, the homogenity and density of the coating will be low therefore at 2 hours holding the hardness value trend that is show more unstable than the 6 hours holding time because with high homogenity the hardness value at each point taken will be close amount at each other.

The hardness value for each specimen is as shown in the Table 4 and if the grade is multiplied it will affect the hardnessand homogenity obtained with the same material.

IV. CONCLUSION

From the research conducted, the conclusion can be drawn regarding the effect of the holding time on the formation of niobium-vanadium carbide coating onto AISI 420 by Thermo Reactive Diffusion process as follow : (1)The thickness of the layer of Niobium-Vanadium carbide (NbVC) formed on the surface of the specimen is affected by the increased of the holding time given Thermo Reactive Diffusion process with the result of the holding time of 6 hours with an average thickness value of 6.95 µm followed by the holding time of 4 hours with average thickness value 6.20 µm, and finally the holding time of 2 hours with average thickness value 5.42 µm; (2)Longer holding time resulted in higher hardness as observed in 2, 4 and 6 hours providing 976.8 HV , 991.1 HV, 13333.2 HV respectively. This value is more than double of uncoated sample which had hardness of 528.6 HV.

DAFTAR PUSTAKA

[1] A. S. M. I. H. Committee, *ASM handbook: Heat Treating*, vol. 4. Asm Intl, 1991.