Microstructure and Micro-Hardness of Al_2O_3 - TiO_2 Coating by Plasma Spraying on SKD61 Steel

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In this research, the modified surface is created by cladding Al_2O_3 particles with 40% TiO_2 particles on an SKD61 steel surface by plasma spraying method. The results indicated that the macrograph of the coating has no cracks, and the coating has an undulating flatness with relatively dark color and distribute uniformly. The coating surface can be divided into three distinct regions: the coating zone, the heat-affected zone, and the SKD61 steel substrate. The coating zone presents a smooth surface and does not have any porous inside it, indicating a good coating film. The microstructure of Al_2O_3 -40% TiO_2 coating mainly consists of plasma-spray stacked layers, includes two regions, in which Al_2TiO_5 phase appeared as gray regions while γ - Al_2O_3 and α - Al_2O_3 particles appeared as white regions. The micro-hardness distribution of the coating showed that the average hardness of the Al_2O_3 -40% TiO_2 coating reaches the highest number with 816.3 $\text{HV}_{0.1}$, while the heat-affected zone gains a hardness number of 595 $\text{HV}_{0.1}$. Both of these zones' hardnesses are greatly higher than the hardness of the SKD61 steel substrate with 252.5 $\text{HV}_{0.1}$. [doi:10.2320/matertrans.MT-MN2019024]

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1. Introduction

In recent years, parallel to the development of surface science and technology, the requirement for improving a product's surface quality and lengthening a product lifetime has remained a major concern. Especially in heavy industries, where machine components always operate in tough environments involving high humidity, high temperature, dust, chemicals. These conditions lead to abrasion, corrosion and finally, failure of machine components. Typically, a hot die is made from a high-strength material so that it could work under high-pressure conditions. While, its surface must have high hardness, high abrasive resistance, and good thermal fatigue at high temperatures to remain the die shape and preserve the product's precision. Whenever the machine components are abraded or corroded there are high costs for disassembling, fixing, reassembling and other costs caused by the stop of the production line.^{1,2)}

Several surface methods are usually used to create layers that meet the complex requirements of different metallic machine parts, such as intense pulsed laser beam,³⁾ electron beam⁴⁻⁷⁾ and ion beam.^{8,9)} Among those methods, plasma spraying method posses a great interest and proving its advantages to other coating methods.¹⁰⁻¹²⁾ This method generates a coating layer that having a high resistance ability to abrasion, corrosion, and high temperature. Moreover, this coating can also be easily replaced and repaired, leading to increase productivity, reduce costs compared to other traditional coating methods. This type of coating has been proved to be appropriate for fixing and restoring mechanical details such as fixing casting defects, recovering worn crankshaft and cylinder.^{13,14)}

Additionally, plasma spraying technique is a thermal spraying process that can create a high-quality coating with high operation speed using a high-energy heating source to

melt the mixture and inert gas to protect the spraying zone. The plasma spraying method can produce heat resistant and conductive layers on non-conductive materials. This method can also product layers that resistance to corrosion for steel structures working in oxidative or electrochemical corrosion environments. Specifically, this technique can also deposit a layer of non-ferrous metals/alloys that are often very expensive on the surface of other low-cost metals. These types of layer could save costs or increase aesthetic value in decorating. For machine components that work in abrasive conditions, their surface coatings should be covered which resist abrasive particles such as TiC , WC , TaC , SiC , CrC , NiCr , Al_2O_3 , TiO_2 , ZrO_2 and Y_2O_3 with customized thickness.^{15,16)} Among them, Al_2O_3 - TiO_2 materials with high-strength and great heat resistant characteristics are superior materials for improving the working ability of SKD61 steel.^{17,18)}

2. Experimental

2.1 Materials and experimental methods

JIS SKD61 steel is selected for the experiment, with a size of $10 \times 12 \times 10$ mm. Table 1 presents the analysis result of atomic emission spectroscopy, showing that the compositions of the steel sample used in the experiment fit the standard of SKD61 steel. The coating materials are Al_2O_3 - TiO_2 with TiO_2 percent is 40%. The information of these material properties can be observed in Table 2.

The heat treatment process was performed at Minh Hanh Company (Fig. 1). The sample is heated gradually at a rate of $220^\circ\text{C}/\text{hour}$, following two holding stage, as shown in Fig. 2. The quenching temperature is chosen at 1030°C to obtain austenite phase, the holding time was 9.6 minutes to finish the austenite phase transformation and achieve a uniform austenite phase. After that, the sample is quenched in the air. The tempering process was performed with an average temperature of 500°C and the samples was hold for

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Table 1 Chemical composition of SKD61 steel sample used in the experiment.

Element	C	W	Ni	Si	Cr	Mo	Ti	P	Mn	V
%	0.327	0.023	0.131	0.9	5.58	1.37	0.004	0.02	0.266	0.802

Table 2 Material properties for Al_2O_3 , TiO_2 and SKD61 steel.

Properties	Al_2O_3	TiO_2	SKD61
Density (g/cm^3)	3.97	3.5 ~ 4.2	7.80
Melting temperature ($^\circ\text{C}$)	2072	1843	1427
Coefficient of thermal expansion ($10^{-6}/^\circ\text{C}$)	8.1	9	12.4
Modulus of elasticity (GPa)	300	230	210

Fig. 1 Heat treatment furnace at Minh Hanh heat treatment Company.

Fig. 2 Heat treatment diagram.

1.5 hours to produce a tempered martensitic structure and achieve an appropriate hardness. Thereafter, the samples are cooled in the air.

Before coating, the sample's surface is made rougher by spraying brown abrasive Corindon beads by Hai Duong Grinding Stone Joint Stock Company to increase the bonding ability with the coating. The roughness spray parameters were: spray distance 200 mm, air pressure 8–10 atm. The plasma spraying process for Al_2O_3 –40% TiO_2 coating was made at the Institute of Tropical Technology, Vietnam

Fig. 3 Molding hot sample method and equipment.

Academy of Science & Technology, with the main parameters: current 550 A, 24 V voltage, Ar gas flow 60 l/min, H_2 gas flow 8 l/min, powder feeding rate 50 g/min, spray distance 120 mm, coating thickness 1 mm~1.3 mm. Normally, the current is selected in a range of 300–725 A. In this case, the current is chosen high enough to melt down the high-melting temperature of the mixture powder of Al_2O_3 –40% TiO_2 , control the porosity and increase the deposition efficiency. The voltage is selected to fit with the current. The optimal Ar and H_2 gas flow is selected to prevent oxidation and porosity. The spray distance should not be too small to cause the thermal effect on the substrate, and also cannot be too large to incompletely meltdown the powder and create porous. Finally, the powder feeding rate is selected to be suitable for equipment power.

2.2 Methods for determining the mechanical properties

The microscopic structure is investigated in the laboratory of D.V.G company. Initially, the laser fiber cutting machine is used to cut samples, with a size of $10 \times 10 \times 10$ mm. The section is perpendicular to the scanning direction of the spray gun. Then, a specialized machine of Buehler company is used to mold the samples with suitable temperature and pressure to create the epoxy covered samples, in order to protect the section of the sample during the polishing process, as illustrated in Fig. 3. Finally, before observing in a microscope, the sample's surface is polished by abrasive paper, polished and then etched by HNO_3 3% in alcohol.

The sample's hardness is measured by HMV-WIN type, with a load of 1.961 N ($\text{HV}_{0.1}$), the stopped-time is 15 s. The bonding zone between the coating layer and SKD61 steel plays a role as the origin point. Then, the hardness above and below the origin is measured, in which the top origin is a positive value and vice versa.

3. Results and Discussion

3.1 Analysis of the surface morphology

Figures 4 and Fig. 5 present the coated sample and the

Fig. 4 Surface morphology.

Fig. 5 Macrograph structure of the coating from the cross-section of Al_2O_3 -40% TiO_2 coating.

macrograph structure of the sample's cross-section, respectively. Figure 5 shows that the coating has an undulating surface, dark color and distributes uniformly. No cracks can be found in the coating. The thermal expansion coefficient of Al_2O_3 -40% TiO_2 coating and alloy steel SKD61 is quite similar. This is very beneficial for reducing thermal stress and the formation of cracks results in generating a high-quality coating.

3.2 Geometric forms of the coating cross-section

Figure 6 demonstrates the cross-section of Al_2O_3 - TiO_2 coating. The results shows that the sample has three different regions: a coating zone, a heat-affected zone, and an SKD61 steel substrate. The coating zone is smooth and has no porous, proving a high-quality coating.

Fig. 6 Cross section of Al_2O_3 - TiO_2 coating. Fig. 7 Macroscopic structure of Al_2O_3 -40% TiO_2 coating.

Figure 7 indicates the macroscopic structure of the coatings. Between the substrate steel and the coating, there is a clear bonding zone with black color. This rough boundary is created during the sandblast step in order to increase the bonding strength between the coating layer and the steel substrate. The microstructure of SKD61 steel after annealing is tempered martensite (needles martensite) and other types of fine carbide. However, in the heat-affected zone, the martensite particles are bigger. The reason is the substrate steel was absorbed huge thermal sources from plasma, so grain boundaries were moved leading to the phenomenon of a larger grain swallow a smaller one. The bonding layer thickness varies from 5 to 15 μm . The bonding layer provides good adhesion and good bonding strength between the substrate and the coating layer.

3.3 Microstructure

Figure 8 indicates the SEM microstructure of Al_2O_3 -40% TiO_2 coating. The structure of the coating mainly consists of plasma-spray stacked layers. Each layer includes two regions, the white and gray zones. According to Cui *et al.* report,¹⁵⁾ the gray region mainly contains Ti, O, and Al, whereas the white region consists of Al and O. The coatings consist of γ - Al_2O_3 , Al_2TiO_5 and little amount of α - Al_2O_3 .¹⁾ As mentioned above, the powder used in the plasma spraying consists of initial injection Al_2O_3 powder and TiO_2 . In the melting and then rapid solidification of the plasma process, most of the Al_2O_3 particles are molten and transform into the γ - Al_2O_3 phase due to the γ - Al_2O_3 phase has lower energy nucleation. However, some of the Al_2O_3 particles had not

Fig. 8 SEM microstructure of Al_2O_3 -40% TiO_2 coating.

Fig. 9 Distribution curve performs microhardness of Al_2O_3 -40% TiO_2 coating.

molten yet, so they are still in the α - Al_2O_3 phase. In addition, Al_2O_3 and TiO_2 are mixed before plasma injection. The melting temperature of TiO_2 is lower than that of α - Al_2O_3 , which are 1854°C , and 2040°C , respectively. During the plasma injection process, due to the ultra-fine size of these particles, the contact area between the two oxide particles is quite large, therefore they react with each other to form Al_2TiO_5 . In conclusion, it is considered that the Al_2TiO_5 phase appeared as gray regions while γ - Al_2O_3 and α - Al_2O_3 particles appeared as white regions.

3.4 Microhardness of the coating

Figure 9 illustrates the microhardness distribution of the Al_2O_3 -40% TiO_2 coating. Generally, the hardness of the coating can be divided into three distinct regions: the heat-affected zone, the bonding zone, and the coating zone. The average hardness of the initial SKD61 steel, the quenched SKD61 steel, and the coating are $252.5 \text{ HV}_{0.1}$, $595 \text{ HV}_{0.1}$, and $816.3 \text{ HV}_{0.1}$, respectively. The coating hardness is greatly higher than both the initial SKD61 steel and the quenched SKD61 steel. The hardness significantly increases from the substrate to the top of the coating, meaning the abrasive resistance of the sample is correspondingly improved. This result proves that after applying plasma spraying, the surface hardness of SKD61 steel was significantly enhanced.

The hardness number of the bonding zone is lower than the coating zone. The reason is the diffusion of Fe atoms in the SKD61 substrate into the bonding zone in the melting process, under the thermal effect of the plasma beam. In this process, the Fe element has an unexpected effect of diluting to other hardening components, so the bonding zone hardness is reduced. The heat-affected zone hardness has the same as the substrate material. The main reason is in plasma spraying processing, the temperature of the heat-affected zone increases as high as the tipping point A_{C3} , then the temperature drops suddenly, this is seen as the heat-affected zone is quenched again.^{15,17} The hardness of the coating is highly enhanced because the new γ - Al_2O_3 phase is formed with high hardness and high melting point.¹⁸

4. Conclusion

This paper investigates the SKD61 steel surface coated by Al_2O_3 particles with 40% TiO_2 powder, using the plasma spraying method. Some results can be withdrawn as follow:

- The macrostructure of the coating has an undulating surface, dark color and distributes uniformly, not any cracks can be found in the coating.
- The coating can be divided into three distinct regions: the coating zone, the heat-affected zone, and the SKD61 steel substrate. The coating zone has a high-quality with a smooth surface and no porosity.
- The microstructure of Al_2O_3 -40% TiO_2 coating mainly consists of plasma-spray stacked layers, includes two regions, in which Al_2TiO_5 phase appeared as gray regions while γ - Al_2O_3 and α - Al_2O_3 phases appeared as white regions.
- The average hardness of the coating is $816.3 \text{ HV}_{0.1}$, which is much higher than the hardness of SKD61 steel and quenched SKD61 steel are $252.5 \text{ HV}_{0.1}$ and $595 \text{ HV}_{0.1}$ respectively.

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