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The Research on the Formation Mechanism of Carbon Deposition Based on Remanufacture Cleaning

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ABSTRACT: In the process of remanufacturing cleaning, the carbon deposition was difficult to remove, this paper wants to provide the basic theory about the carbon removal. In this paper, the chemical composition and the microstructure of carbon deposition were analyzed, so as to get the microscopic structure of carbon deposition. Analyzing the formation reaction, adhesion process and the contribution of different electrostatic forces to the formation of carbon deposition. At last, explaining the reasons of the formation of carbon deposition.

KEYWORDS: Remanufacturing; Carbon deposition; Adhesion mechanism; Electrostatic force.

1 INTRODUCTIONS

Remanufacturing cleaning is one of the most important steps in the process of mechanical products remanufacturing, which is the basic requirement for the machining before the detection and renovation to the most parts, and which is also the basement of mechanical products remanufacturing. As we know, engine is a crucial part for the machines, and in the process of its all-life-long working, it will produce a kind of dense black oily substance sticking to the engine combustor and engine valve, which is difficult to remove. This kind of substance is called engine carbon deposition. The composition of carbon deposition is so complex that contains varieties of inorganic and organic substances, including incompletely burned lubricating oil and fuel, the dust from the air and small particles produced during the normal work of the engine. In the process of remanufacturing, due to its complex composition and strong adhesion, the carbon deposition inside the engine becomes an important cleaning object in the process of cleaning.

The traditional remanufacturing cleaning methods are also limited, such as water jet cleaning technology, chemical cleaning technology, blasting/peening technology, dry ice cleaning technology, ultrasonic cleaning technology. Water jet cleaning cannot clean the complex surface tidily. Chemical cleaning agents usually do great harm to the environment. Blast cleaning technique is a physical cleaning method, but the huge disadvantage of noise, etc. [1]

Remanufacturing has become an important part for national energy conservation, mitigation resources and environmental crisis, the development of circular economy [2, 3]. The method to remove the carbon deposition is mainly high temperature thermal decomposition and blast cleaning technology, however this kind of method is relatively high energy consumption, and pollutes the environment terribly [4]. What's more, the research on the remanufacturing cleaning is facing the technology bottleneck for the realization of high efficient, environmental and low cost in the cleaning process. Therefore to carry out the research on the key scientific issues of the formation of carbon depositions and other pollutants, meeting with the national development of the major demand for manufacturing strategy. It is meaningful for our country to realize the rapid development of remanufacturing industry, raise the level of remanufacturing and international competitiveness, and promote the sustainable development of the national economy.

Figure 1. Carbon deposition of the valve and cylinder.

Currently many people are working on the carbon deposition researching, Ma hailin mainly analyzed the formation reason of carbon deposition in the aspects of fuel and intake air [5], Chen zhaowen mainly researched the chemical composition [6], Diaby M teammates researched the influence factors of carbon deposition in the aspects of temperature, pressure and time [7]. So it is very important for remanufacturing cleaning technology optimization to research the formation mechanism of carbon deposition and microstructures.

2 THE BASIC PROPERTY ANALYSIS ON CARBON DEPOSITION

2.1 *Chemical composition analysis on carbon deposition*

Table 1. Elements and its weight fraction in carbon deposition.

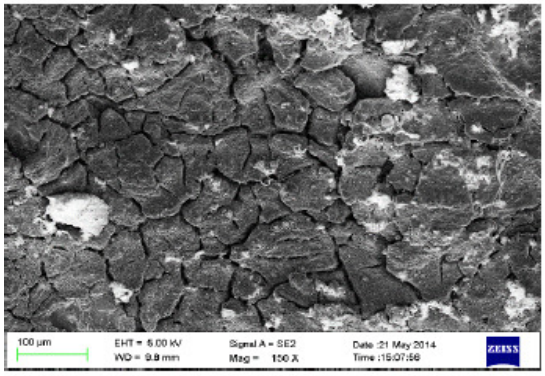
element	O	C	Mg	Al	Si	P	S	Fe	Zn
quality fraction/%	36.90	29.80	1.11	0.71	1.22	4.92	3.71	10.83	10.80
mass fraction /%	41.66	44.81	0.83	0.48	0.78	2.87	2.09	3.50	2.98

It can be seen from table 1 that the main substances in the carbon deposition are the elements O and C, this confirms that the chief process of carbon deposition is the reaction between C and O. Meanwhile, the element Si is a little more than it should be, this is because the air the engine intakes contains some dust particles. And there are also some metal elements like Fe, Al, Mg, which are the small particles produced by normal wear. The P, S elements are from the additive in the fuel oil and lubricating oil.

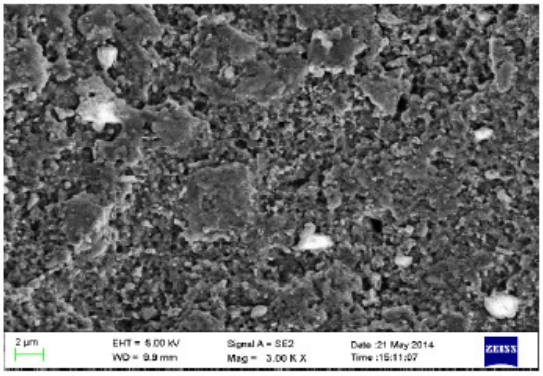
With the infrared spectroscopic analysis, we find that there are many OH groups, carboxyl groups, amidogens and carbonyl groups in the carbon deposition, which will lead to the formation of macromolecular organic substance.

2.2 *Carbon deposition microstructure researching*

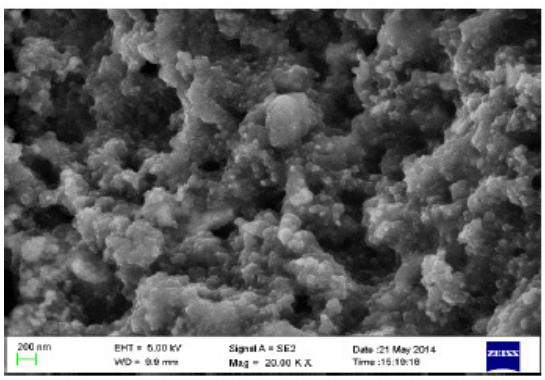
In this paper, the surface morphology of carbon depositions was observed by hot field emission scanning electron microscopy (Carl Zeiss Company. German, type: SUPRA55) in different times.



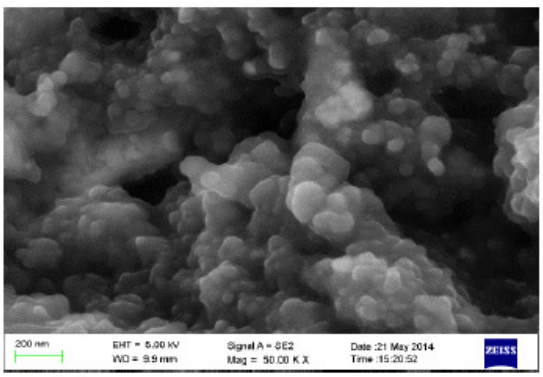
(a) the form of Carbon deposition at 150X



(b) the form of Carbon deposition at 3KX



(c) the form of Carbon deposition at 20KX



(d) the form of Carbon deposition at 50KX

Figure 2. Carbon deposition morphology.

By using this kind of electron microscopy, we can see from the Figure 2 that there are a lot of small cracks on the surface of carbon deposition in 150 times magnification. Under 3000 times magnification, we can see white particles covered on the surface. In multiples of 20 thousand, the surface of carbon deposition is not smooth but uneven, and there are a lot of holes whose shapes are complex. In more details, the diameter of holes range from 200nm to 800nm. When the particles are observed in 50 thousand times, the shiny parts are small carbon particles newly formed. The irregular morphology of the surface increases the contact area of carbon depositions and gas in the combustor. What's more, the complex holes increase the admissible space for the large molecular particles generated by carbon deposition. The surface of the carbon deposition increases the capture force for carbon particles and metal particles.

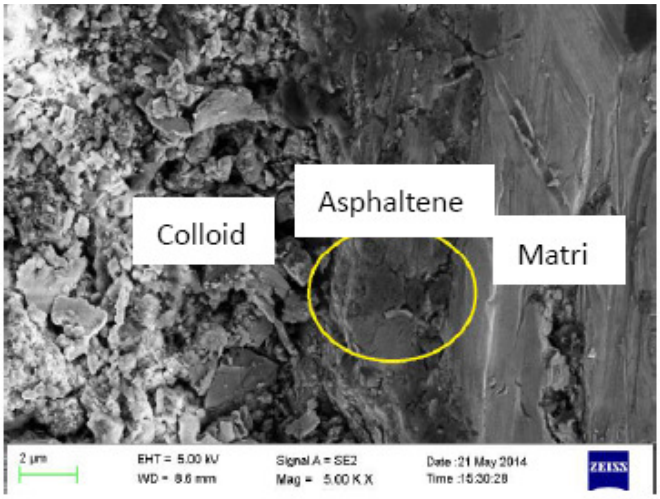


Figure 3. Carbon deposition layer structure.

The carbon deposition with layered structure (Figure 3) can be observed clearly in the microscope of 5 thousand times. The layer of colloid is porous, the granular solids can be clearly seen, whose diameter ranges from 0.5 to 3 micron and it mainly contains small particles of wear metal and newly developed carbon particles. The layer of asphaltene is more compact, which is tightly adhered to the matrix, there is a clear dividing line with colloid. By the above observation, it can be drawn that the structure of the surface of carbon deposition will play an incentive role to new carbon deposition, without timely removal, it will reduce the volume of the combustor, increase the compression ratio, and engine blow out or even worse. Therefore to the engine remanufacturing, the combinational layer between asphaltene and matrix should be focused in the process of cleaning.

3 THE ANALYSIS ON THE FORMATION MECHANISM OF CARBON DEPOSITION

3.1 *The chemical reaction of carbon deposition*

The carbon deposition in the engine mainly comes from the incompletely burned fuel and lubricating oil. When the supply of oxygen to the engine is insufficient, the incompletely burning will happen, and lead to the initial particles of carbon deposition. These particles will continue to the oxidation reaction in the engine. When the oxygen supply is excessive, the fuel oil and residual lubricating oil will be promoted to the further react in the strong oxidizing, high temperature and high pressure environment, producing a variety of small-molecule substances, such as the primary oxidation products of aldehydes, ketones, acids, alcohols, etc.

This paper analyzes as following based on the mechanism of initial formation of carbon deposition in the engine. (RH represents the organics of H element, R" represents the decomposition products of organics, ROO" represents the oxidation products of organics):

Step one: $RH \xrightarrow{\Delta} R" + H"$

$R" + O_2 \longrightarrow ROO"$

Step two: $ROO" + RH \longrightarrow ROOH + R"$

$ROOH \longrightarrow RO" + HO"$

$RO" + RH \longrightarrow ROH + R"$

Step three: $HO" + RH \longrightarrow H_2O + R"$

Step four: $R"+R"$, $ROO"+R"$, $ROO"+ROO"$, $RO"+R"$ $\longrightarrow$ aldehydes, ketones, acids

This is consistent with the analysis of infrared spectrum, which confirms that the carbon deposition is composed of the organic macromolecules.

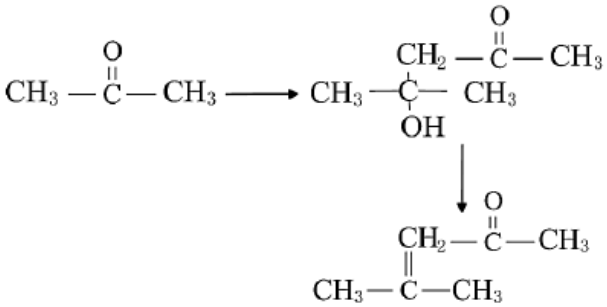


Figure 4. Polymerization reaction of primary oxidation product.

Small organic molecules will continue to the reaction of addition polymerization and condensation under the catalytic role of metal particles and the high temperature and high pressure environment in the engine. There are many unsaturated bonds (double bonds, triple bonds, conjugated double

bonds) in the organic molecules, which will react with the other similar structures then form a new chemical bond, connected to form a long chain, or lose the inorganics or water to produce the small molecules. At the temperature of 225℃, the content of phenol decreases, produces the aldehydes and ketones. When the temperature is higher than 350℃, if the oxygen is sufficient, the hydrocarbons will change into aromatic hydrocarbon with the influence of cyclization. Figure 4 is an oxidation process.

3.2 *The adhesion mechanism of carbon deposition*

The process of adsorption is that the organic molecules doing the Brownian motion get together to the surface under the effect of the electrostatic force, the van der waals, hydrogen bond, etc.

Metal particles are produced during normal operation of the engine, which will be the catalyst to promote small molecules to the reaction, and format the large molecules after polymerization and condensation reaction. Larger molecules will gather and be attached on the surface of parts when combined with small metal particles. Under such circumstance, it gradually formed a porous colloid layer, which is very viscous. With its special structure it will constantly adsorb the burned carbon particles, the lead in the antiknock agent that added in the gasoline is produced by combusting, the metal oxide generated by the adding metal additives in lubricating oil, the dust particles in the air the engine intakes and the sulfate, etc. Under the environment of high temperature and high pressure, the colloid layer is compressed constantly, and the structure of pores is reduced continuously, at last, it is squeezed into the asphaltene layer, forming the carbon deposition with complex composition and compact structure.

In the previous studies, the carbon deposition is usually regarded as a process of continuous accumulation on the surface of the solid. In fact, the whole process of adhesion is similar to the process of colloidal bonding including the substances of carbon particles, metal particles, and complete combustion of lubricating oil and fuel. It is an unbalanced thermodynamics and dynamics process driven by a variety of effects of physical chemistry.

According to the adhesion process of carbon deposition, the force of the adhesion can be divided as following:

(1) Intermolecular atomic force: London dispersion force, dipole and induced dipole force, etc.

(2) Hydrodynamic Interaction: With the constant motion of the air in the high temperature and high pressure environment in the cylinder, it will produce the carbon layer continuously, make the surface roughness, and increase the area to "capture" the carbon deposition molecules.

(3) Electrostatic force: metal oxide and metal hydroxide particles generally positively charged, non-metallic oxides, some acid particles and sulfide colloid formed by explosion-proof agent are the negatively charged particles. These two kinds of particles will gather constantly by the electrostatic force, forming the larger particles.

(4) Chemical bond force: it is very easy for small molecule particles to react under the catalysis of metal particles, high temperature and high pressure environment. The new chemical bond is formed by the interaction between saturated bond and unsaturated bond, which can increase the cohesive force between the molecules of the carbon, and will be adhered on the surface of the matrix.

4 CONCLUSIONS

Based on the analysis of the hot field emission scanning electron microscopy and infrared spectrum, this paper comprehensively studies the composition and morphology of carbon deposition, and main components of carbon deposition and the structures of the carbon deposition are obtained.

Based on the components and the structures of the carbon deposition, this paper puts forward the chemical equation of the carbon deposition, establishes the adhesion mechanism of carbon deposition, and analyses the effect of the electrostatic force, the van der waals, hydrogen bond.

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