

STUDY ON THE pH VALUE REGULATOR OF FERRIC CHLORIDE BASED SLURRY IN CHEMICAL MECHANICAL POLISHING 304 STAINLESS STEEL

Su JIANXIU^{1*}, Peng YANAN², Liu ZHENHUI³, Li JIEJING⁴, Chen JIAPENG⁵,
Li YONGFENG⁶

Due to its good properties, stainless steel is a promising material to be used as substrate for the development of large size flexible display, and the chemical mechanical polishing (CMP) is one of the most practical processing technologies to be used to achieve the surface of the stainless steel materials with highly smooth surface and without damage. In this paper, the authors have investigated the influence of the pH value and the pH value regulator on the material removal rate (MRR) and surface roughness by using the CMP technology with the ferric chloride based polishing slurry. The experimental results show that the MRR increased with the decrease of the pH value and the surface roughness decreased with the decrease of the pH value. Under the experimental conditions, when pH=2, the MRR reached the maximum. The different pH regulator has the different influence on the material removal rate and surface roughness. Under the same conditions, it can achieve the maximum material removal rate and low surface roughness when adjusting the pH value of the slurry using the oxalic acid. So the best pH value regulator is the oxalic acid. These research results in this paper can provide a reference for further research on chemical mechanical polishing the 304 stainless steel.

Keywords: 304 stainless steel, chemical mechanical polishing, polishing slurry, pH regulator, material removal rate

¹ School of Mechanical and Electrical Engineering, Henan Institute of Science and Technology,

Xinxiang, China, e-mail: dlutsu2004@yeah.net

² School of Mechanical and Electrical Engineering, Henan Institute of Science and Technology, Xinxiang, China, e-mail: 49901447@qq.com

³ School of Mechanical and Electrical Engineering, Henan Institute of Science and Technology, Xinxiang, China, e-mail: 1047976972@qq.com

⁴ School of Mechanical and Electrical Engineering, Henan Institute of Science and Technology, Xinxiang, China

⁵ School of Mechanical and Electrical Engineering, Henan Institute of Science and Technology, Xinxiang, China

⁶ School of Mechanical and Electrical Engineering, Henan Institute of Science and Technology, Xinxiang, China

1. Introduction

Because of its many good performances, such as ultra-thin, lightweight, durable, large storage capacity, design freedom, flexible, rolling and impact resistant [1-2], flexible display will be widely used in industrial, civil and military industries in the fields of mobile phones, the personal digital assistant PDA, etc[3-4]. Many research institutions and manufacturers in many countries and regions have joined into the research and application of flexible display technology [5-6]. In recent years, many companies have produced out the foldable or flexible organic light-emitting diode (OLED) screen continuously [7].

Because the flexible display must have the flexible and rolling functions, the substrate of flexible display should be a flexible material. Before making the device, the surface quality of the flexible substrate must be highly smooth and damage free. The surface roughness, usually denoted by the profile arithmetic mean deviation (R_a), of the flexible substrate must be less than 5nm and its waviness must be less than 0.1 μ m. The material of the flexible substrate should have another good performance, such as the high thermal stability, high strength with lightweight, thin, high flexibility, toughness and so on. The 304 stainless steel materials have these performances above-mentioned and the low cost, so, it will become the main substrate material in large size flexible display in the future [8-9]. But the machining quality and precision of the ultra-thin stainless steel sheet will directly affect the performance of the flexible display device [10]. When the surface of the thin stainless steel sheet has some small defects, these defects will be genetic onto the film in the process of the epitaxial growth and it will lead to the fatal defects on the device. Therefore, how to effectively obtain the large size flexible display substrate with the high quality and the high precision and meet the requirements for flexible displays in the present and future, this is a first priority in the flexible display industry at present [11].

Many domestic and foreign scholars have studied largely and deeply on the polishing technology of the stainless steel material. The main polishing methods are mechanical polishing, chemical polishing, electrochemical polishing and electrochemical mechanical polishing, etc [12]. The surface roughness R_a and the depth of the damage layer polished using mechanical polishing; chemical polishing and electrochemical polishing often were very large and could not meet the requirements [13-14]. The surface roughness R_a and the depth of the damage layer polished using electrochemical mechanical polishing could meet the requirements, but the device of electrochemical mechanical polishing is very complex, the polishing parameters are very difficult to be controlled and the surface quality is unstable because of the influence of current fluctuation [15].

Chemical mechanical polishing (CMP) technology has been considered as the best method to meet both the surface roughness and surface flatness and has become one of the most useful processing techniques to achieve the surface of

hard brittle crystal materials with ultra smooth and damage free. It has been widely used in large scale integrated circuit, semiconductor lighting and other fields [16]. The CMP technology may be the most suitable method to be used in the high efficiency and the ultra precision machining for large-size ultra-thin stainless steel flexible display substrate, and to obtain the surface with ultra smooth and damage free.

Only a few literatures about the study of CMP stainless steel had been found. The literature [17] had studied the influence of the temperature on the polishing surface quality in chemical mechanical polishing of stainless steel. Our research group [18-20] have studied the CMP slurry and CMP process of the stainless steel, respectively. There is no other literature to be found to report for machining the stainless steel using the CMP method.

In the CMP process, the slurry is one of the most important components and the cost of the CMP slurry is about 60% to 70% in the total cost of chemical mechanical polishing. So, the ingredients of CMP slurry will determine the efficiency, the quality and the cost of chemical mechanical polishing. Therefore, it is urgent to study CMP slurry of stainless steel with the environmental protection and high efficiency. The pH value is an important index in the CMP slurry, which can provide a suitable environment for the chemical reaction with the polished surface material, and maintain the material removal. Therefore, it is urgent to study the slurry of the environmental protection and high efficiency in CMP stainless steel.

In order to study the CMP slurry of stainless steel, in this paper, a series of experiments, the influence of the pH value on the material removal rate (MRR) and surface roughness had been studied with the CMP slurry of the ferric chloride oxidizing type. According to the experimental results, the optimum pH value and the best pH value regulator had been selected in CMP 304 stainless steel with different slurry. These results will provide a reference for further study on the CMP slurry of the 304 stainless steel.

2. Experiments preparation and experimental parameters

2.1 Sample preparation

All the CMP experiments were carried out in the clean room with grade 1000, and the environmental temperature was controlled at 22 °C, and the water used in the all experiments was ultra-pure water with the electrical resistivity 18.24 MΩ·cm. Many of experimental samples for 304 stainless steel sheet with 3 mm in thickness and 50 mm in diameter was used in CMP experiments. Before the experiment, these samples were fine lapped and the surface roughness Ra is in 40 nm to 50 nm after lapping. The CMP experiments were carried out on the

polishing machine ZYP300 type produced by Shenyang. The type of CMP pad used is Rode IC1000.

2.2 CMP parameters

The rotational speed of the polishing platen and the carrier is set 60 rpm, the CMP pressure P is set to 13789.55 Pa, and the CMP time is set to 15 min. The polishing pad must be conditioned every time after CMP and conditioning time is set to 15 min. In the CMP process, the carrier oscillates reciprocating along the arc with the oscillation frequency 10 s and the oscillation amplitude 20 mm. The center distance between the carrier and polishing platen is set to 80 mm.

2.3 Characterization methods

Testing instruments used in the experiment. The precision balance (accuracy 0.01 mg) of Sartorius CP225D was used to test the weight of the sample before and after CMP, and then the material removal rate can be calculated by the weight removed. The 3D microscope Contour GT-K (vertical resolution 0.01 nm) produced by BRUKER corporation of the United States was used to measure the surface roughness and surface morphology of the samples before and after CMP. The metallographic microscope with Lecia DM2500M was used to detect the 2D surface original image before and after CMP. The laser particle size distribution instrument with JNGX JL-1197 was used to test the distribution of abrasive in polishing slurry. The pH test pen (precision 0.1) was used to test the pH value of slurry.

2.4 The basic components of polishing slurry

According to the characteristics of the 304 stainless steel material and the orthogonal test results of polishing slurry former researched, the alumina is selected as the experimental abrasive with the diameter 3.5 μm and the content 4.5 g, the nitric acid and the sodium hydroxide was selected to adjust pH value of slurry on the level of 2, 4, 6, 9, 11 and 13 with different content of oxidant, the glycerol was selected as the dispersant with the content 3 g. Taking the ferric chloride as the oxidant and the content of the ferric chloride takes as 5 g, 10 g, 15 g, 20 g and 25 g with different pH value. Rest is the deionized water. Before the experiments, each kind of slurry with volume 250 ml was freshly prepared. Each CMP slurry with pH value and content of oxidant sees table 1.

Table 1
The component of polishing slurry with pH value and content of oxidant

Slurry serial number	pH value	Content of oxidant(g)	Others
1 to 5	2	5, 10, 15, 20, 25, respectively	
6 to 10	4	5, 10, 15, 20, 25, respectively	Abrasive,
11 to 15	6	5, 10, 15, 20, 25, respectively	dispersant
16 to 20	9	5, 10, 15, 20, 25, respectively	and water

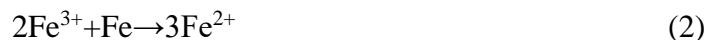
21 to 25	11	5, 10, 15, 20, 25, respectively
26 to 30	13	5, 10, 15, 20, 25, respectively

3. Results and discussions

3.1 The effect of pH value on the material removal rate and surface roughness

Taking the hydrogen peroxide based slurry and FeCl_3 based slurry as the research objects, the influence of the pH value and the pH regulator on the material removal rate and surface roughness had been studied in CMP stainless steel used the different polishing slurry respectively. The pH value of the polishing slurry was adjusted by using nitric acid and sodium hydroxide at 2, 4, 6, 9, 11 and 13 levels in Table 1.

Fig.1 shows the experimental results of CMP 304 stainless steel using the FeCl_3 based slurry. By Fig.1a, it can be seen the effect of the slurry pH value on the MRR and surface roughness when CMP the 304 stainless steel taking the ferric chloride as oxidant. It can be seen that the MRR decrease with the increase of pH value. The change trend is not changed with the content of the ferric chloride in slurry. This illustrates that the MRR is low when CMP with the alkaline slurry and large when CMP with the acidic slurry. Because that the oxidant of the ferric chloride can be decomposed into ferric iron ion and chloride ion in aqueous solution. The ferric iron ion can generate the redox reaction with the iron, nickel and chromium in 304 stainless steel surface material and produce the ferrous chloride to achieve the removal of the stainless steel surface material. The chemical reaction is as follows.



By Fig.1a, when $\text{pH} > 4$, the MRR increases with the decrease of the slurry pH value, but the increase was not obvious. When $\text{pH} < 4$, the MRR increases greatly with the decrease of the pH value. The MRR reaches the maximum when $\text{pH} = 2$. It is illustrated that the chemical reaction of the ferric chloride with 304 stainless steel material accelerates in the strong acid environment. This will accelerate the MRR greatly.

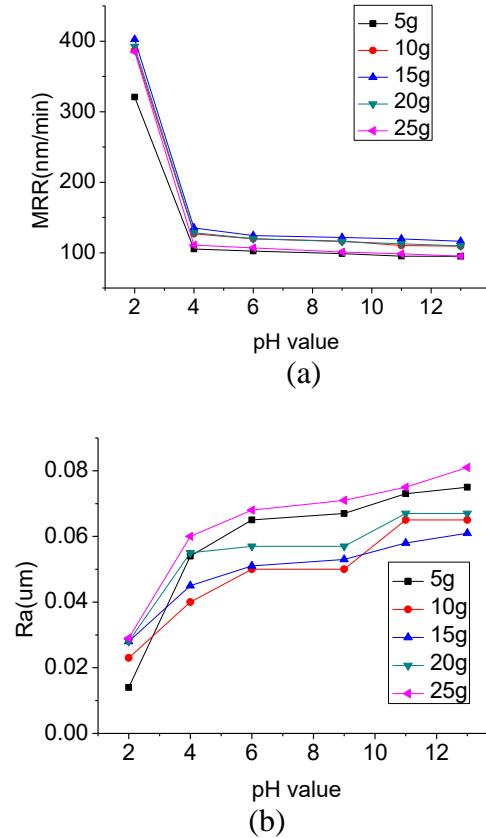


Fig. 1 Experimental results after CMP using polishing slurry with oxidant ferric chloride.
(a) The material removal rate, (b) Surface roughness

In alkaline environment, it can be seen from equation (1), (2), (3) and (4) that the concentration of the OH^- ion in polishing slurry increases with the increase of pH value, then the OH^- ion will react with the H^+ ion in polishing slurry to form the water and decrease the content of H^+ ion, so the balance of the Eq.1 moves to the right and decreases the concentration of the Fe^{3+} ion in polishing slurry. At the same time, the OH^- ion in polishing slurry will react with Fe^{3+} ion to form $\text{Fe}(\text{OH})_3$ and also decreases the concentration of the Fe^{3+} ion in polishing slurry. The above two kinds of cases can both make the balance of the Eq.1 moves to the right, promote the hydrolysis of FeCl_3 , decrease the concentration of Fe^{3+} ion in polishing slurry and reduce the reaction of Eq.2, Eq.3 and Eq.4. This reduces the rate of chemical reaction on the stainless steel surface and reduces the material removal rate. On the contrary, in the acidic environment, the concentration of the H^+ ion in polishing slurry increases with the decrease of the pH value, then break the balance of Eq.1, the increase of the H^+ ion can make the balance of the Eq.1 move to the left. This will prevent the hydrolysis of FeCl_3 ,

increase the concentration of Fe^{3+} ion in polishing slurry and promote the reaction of Eq.2, Eq.3 and Eq.4. Therefore, it will improve the rate of chemical reaction on the stainless steel surface and increase the material removal rate greatly.

Fig.1b shows the surface roughness R_a of the samples after CMP. From Fig. 1b, it can be seen that the surface roughness increases with the increase of the pH value of slurry after polishing and in different content of ferric chloride, when pH=2, the surface roughness of the samples reaches the minimum after polishing.

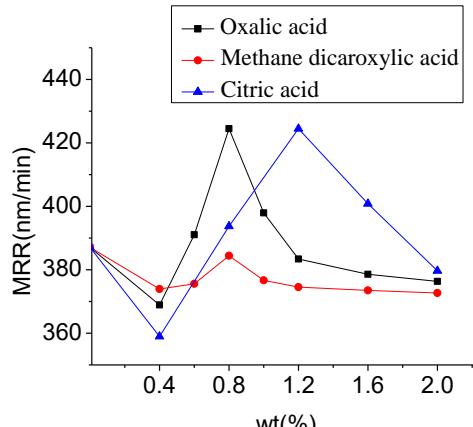
By the above analysis, it can be seen that the smaller the pH value of the polishing slurry, the greater the material removal rate and the smaller the surface roughness under the different content of oxidant, whether it is the hydrogen peroxide or the ferric chloride.

3.2 Effect of the species of pH regulator on the material removal rate and surface roughness

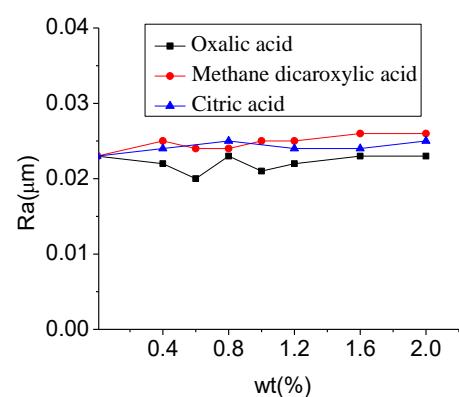
According to the above research results, it can be seen that the pH value of the slurry CMP 304 stainless steel should be less than or equal to 2. A lot of acid can be used as a pH value regulator. These commonly used are the nitric acid, phosphoric acid, acetic acid, oxalic acid, citric acid, methane dicarboxylic acid, etc. Which is the most appropriate pH regulator, it needs to carry out the experimental study.

Because the ferric chloride is a sort of strong acid, by the literature and analysis, three kinds of organic acids, oxalic acid, methane dicarboxylic acid and citric acid, had been researched as the pH regulator for ferric chloride based polishing slurry. From the table 2, taking the content of the ferric chloride 10g and other ingredients unchanged, a number of the 250ml polishing slurry were prepared each time only changing the pH value. The experimental results were shown in Fig. 2.

By Fig.2a, it can be seen that the maximum of MRR can be achieved at a certain content of above three kinds of organic acid. When at the other content, the material removal rate is lower. When the content of the oxalic acid, the methane dicarboxylic acid and the citric acid was 0.8 wt%, 0.8 wt% and 1.2 wt% respectively, the material removal rate reached maximum, they were 426 nm/min, 388 nm/min and 425.3 nm/min respectively.



a)



(b)

Fig.2 Experimental results of pH regulator for the ferric chloride based slurry.
 (a) Material removal rate, (b) Surface roughness, R_a

By Fig.2b, when taking the oxalic acid as the pH regulator, the surface roughness is lower after CMP. Therefore, according to the comprehensive analysis, it is the best choice the oxalic acid as the pH regulator for ferric chloride based polishing slurry and the concentration is about at 0.8 wt%.

In these three kinds of organic acids, the oxalic acid, the methane dicarboxylic acid and the citric acid, the acidity of the oxalic acid is the strongest, the next is the methane dicarboxylic acid and the acidity of the citric acid is the weakest. Next, the oxalic acid was taken as an example to analyze the role of organic acids as the pH regulator.

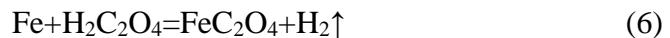
3.3 The chemical reaction of ferric chloride and oxalic acid.

Eq.5 is the reaction equation of the ferric chloride and oxalic acid in CMP slurry. By Eq.5, it can be seen that the oxalic acid can react with Fe^{3+} ion to form Fe^{2+} ion. On the one hand, the number of Fe^{3+} ion decreased and the number of Fe^{2+} ion increased in the slurry. This will reduce the reaction rate of Eq.2, Eq.3 and Eq.4 and the material removal rate decreased. But on the other hand, the H^+ ion from Eq.5 has an etching effect on stainless steel material to improve the MRR in CMP process.



3.4 The effect of oxalic acid and its content.

As the pH regulator, on the one hand, oxalic acid can adjust the pH value of the slurry, on the other hand, the oxalic acid solution have the $\text{C}_2\text{O}_4^{2-}$ (oxalate ions), H^+ (hydrogen ions) and HC_2O_4^- (hydrogen oxalate ions). The $\text{C}_2\text{O}_4^{2-}$ has very strong complexation and can chelate the metal in the stainless steel material, thus, it will promote the material removal, sees Eq.6.



By Eq.5, with the increase of the oxalic acid content, the concentration of H^+ ion in CMP slurry increases and the etching effect of H^+ ion on stainless steel surface increases. On the other hand, with the increase of oxalic acid content, the pH value of the slurry decreases. In lower pH value slurry, this will also restrain the reaction of the Fe^{3+} with oxalic acid and the hydrolysis of FeCl_3 . So the material removal rate increases, because the hydrolysis action of FeCl_3 enhances in the higher pH value environment and leads to decrease the concentration of FeCl_3 in slurry, and reduces the etching effect of Fe^{3+} on stainless steel [21].

When the content of the oxalic acid increases to a certain extent, such as more than 0.8%, the $\rho(\text{H}^+)$ in slurry reaches the potential of hydrogen release. This will produce the hydrogen evolution reaction and reduce the reaction of Fe^{3+} , thus, this will lead to the decrease of the MRR [22].

3.5 Effects of the ferric chloride.

By the analysis result of the above mentioned, on the one hand, with the decrease of pH value in slurry, according to the formula (1), (2), (3) and (4), the hydrolysis action of ferric chloride reduces and the etching effect on stainless steel enhances. This will promote the MRR in CMP process. On the other hand, the Cl^- ion in the slurry can produce the complexation with Fe^{2+} , Fe^{3+} , Ni^{2+} and other

metal ions to form these soluble complex ions, such as FeCl_4^{2-} , NiCl_4^{2-} , FeCl_4^- , etc. and dissolve in the polishing slurry quickly. This will prevent the metal ion after etched to produce a layer of dense oxide film on the surface, then, this will reduce the inhibitory effect of oxide film in the CMP process and improve the material removal rate.

In the above analysis, the material removal is decided by all action result of the above mentioned.

To sum up the above analysis, the oxalic acid is the best one of pH regulators for the ferric chloride based slurry.

4. Conclusions

In summary, through a series of experiments and results analysis, the following conclusions are as follows.

In alkaline environment, the concentration of the OH^- ion in polishing slurry increases with the increase of pH value, but, the OH^- ion will decrease the concentration of the Fe^{3+} ion in polishing slurry, promote the hydrolysis of FeCl_3 and reduce the chemical reaction rate on the stainless steel surface. On the contrary, in the acidic environment, the concentration of the H^+ ion in polishing slurry increases with the decrease of the pH value, then, the H^+ ion will prevent the hydrolysis of FeCl_3 and increase the concentration of Fe^{3+} ion in polishing slurry and promote the chemical reaction rate on the stainless steel surface. On the other hand, in the acidic environment, the Cl^- ion in the slurry can produce the complexation with Fe^{2+} , Fe^{3+} , Ni^{2+} and other metal ions to form these soluble complex ions, so, this will prevent the metal ion after etched to produce a layer of dense oxide film on the surface and improve the material removal rate. Therefore, when CMP 304 stainless steel taking the ferrous chloride as the oxidant of polishing slurry, the lower the pH value of the slurry is, the greater the material removal rate is.

The oxalic acid can react with FeCl_3 to form H^+ ion and the H^+ ion has an etching effect on stainless steel material to improve the MRR in CMP process. With the increase of the oxalic acid content, the concentration of H^+ ion in CMP slurry increases and the etching effect of H^+ ion on stainless steel surface increases. On the other hand, with the increase of oxalic acid content, the pH value of the slurry decreases and in lower pH value slurry, it will also restrain the reaction of the Fe^{3+} with oxalic acid and the hydrolysis of FeCl_3 . At the same time, the $\text{C}_2\text{O}_4^{2-}$ in the oxalic acid solution has very strong complexation and can chelate the metal of the stainless steel material to promote the material removal. So, to the ferric chloride based polishing slurry, the best pH value regulator is the oxalic acid. The maximum material removal rate and low surface roughness can be achieved using the oxalic acid as the pH value regulator.

The research results will provide an important reference for the next step to study the CMP slurry of the 304 stainless steel.

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R E F E R E N C E S

- [1] Logothetidis S, Laskarakis A. Towards the optimization of materials and processes for flexible organic electronics devices [J]. *The European Physical Journal Applied Physics*, Vol.46, No.1(2009), p.12502(1-9).
- [2] Hanada T ,Negishi T, Shiroishi I, et al. Plastic substrate with gas barrier layer and transparent conductive oxide thin film for flexible displays[J].*Thin Solid Films*, Vol.518, No.11(2010), p.3089-3092.
- [3] Ju S, Li J, Liu J, et al. Transparent active matrix organic light-emitting diode displays driven by nanowire transistor circuitry [J]. *Nano.Lett.*, Vol.8, No.4 (2008), p.997-1004.
- [4] Bae S, Kim H, Lee Y, et al. Roll-to-roll production of 30-inch graphene films for transparent electrodes [J]. *Nature Nanotechnology*, Vol.5, No.8(2010), p.574-578.
- [5] Sekitani T, Nakajima H, Maeda H, et al. Stretchable active-matrix organic light-emitting diode display using printable elastic conductors[J].*Nature Materials*, Vol.8, No.6(2009), p.494-499.
- [6] Someya T., Flexible electronics: Tiny lamps to illuminate the body [J]. *Nature Materials*, Vol.9, No. 11(2010), p. 879-880.
- [7] Xu Zheng, SONG Dan-dan, ZHAO Su-ling, et al. The Developments and Challenges in OLED, Flexible and See-through Display Technologies, and Organic Luminescent Materials. *Advanced Display*, Vol. 101, No.6(2009), p. 5-10
- [8] Sugimoto Akira, Ochi Hideo, Fujimure Soh, et al. Flexible OLED displays using plastic substrates [J]. *IEEE J Sel Top Quantum Electron*, Vol.10, No.1(2004), p. 107-114.
- [9] Bardsley J N. International OLED technology roadmap [J]. *IEEE J Sel Top Quantum Electron*, Vol.10, No.1(2004), p. 3-9.
- [10] Xie zhiyuan,Hung Liangsun,Zhu Furong.A flexible top-emitting organic light-emitting diode on steel foil[J].*Chem Phys Lett* , Vol.381, No.5/6(2003),p.691-696.
- [11] Liu Haiyan. Performance and Test of Glass Substrate for TFT-LCD. *Glass*, Vol.36, No.1 (2009), p. 22-24.
- [12] Wang Yue, Man Rui-lin, Liang Yong-huang, et al. Progress in Research on Surface Polishing Technologies for Stainless Steel. *Electroplating & Pollution Control*, Vol.32, No.2(2012), p. 1-4.
- [13] K.P. Han, J.L. Pang. Chemical Polishing for Stainless Steel. *Journal of the Electrochemical Society of India*, Vol.45, No.1 (1996),p.50-52.
- [14] H. Keping, F. Jingli. Study on chemical polishing for stainless steel. *Transactions of the Institute of Metal Finishing*, Vol.76, No.1 (1998), p.24-25
- [15] Yao Ying-Wu,Qiu Li,Zhao Chun-mei,et al. Chemical Polishing Technology of Stainless Steel. *Plating & Finishing*, Vol.32, No.9(2010), p. 5-8.

- [16] Xiaokai Hu, Zhitang Song, Fei Qin, et al. Chemical mechanical polishing of stainless steel foil as flexible substrate. *Applied Surface Science*, Vol.258, No.15(2012), p.5798-5802.
- [17] Zheng Hai-Feng, Wei Xin, Xie Xiao-zhu, et al. Research on process temperature during chemical mechanical polishing of stainless steel substrate. *Diamond & Abrasives Engineering*, Vol.34, No.2(2014), p. 20-24.
- [18] Jianxiu Su, Jiapeng Chen, Haifeng Cheng. Analysis on the influence of oxidant in CMP of ultra-thin stainless steel [J]. *Advanced Materials Research*, Vol.1027 (2014), p. 167-170.
- [19] Jiapeng Chen, Jianguo Yao, Lijie Ma, et al. Study of the Slurry in CMP 304 Ultra-Thin Stainless Steel Surface[J]. *Advanced Materials Research*, Vol.1027 (2014), p.235-239.
- [20] Chen Jiapeng, Chen Shaokun, Li Qing, et al. Study on chemical mechanical polishing of 304 stainless steel sheet based on alkaline polishing slurry. *Diamond & Abrasives Engineering*, Vol.36, No.2(2016) , p.6-9.
- [21] Chen Tianyu. *Surface treatment technology of stainless steel*(Chemical industry press, Beijing 2004, 374- 380)
- [22] Fu Yu-Ting, Ba Jun-Zhou, Jiang Ya-xiong, et al. Influencing Factors on Etching Rates of Stainless Steel[J], *Plating & Finishing*, Vol.32, No.2(2010), p. 34-36.