Int. J. Electrochem. Sci., 10 **(2015)** 6844 - 6854

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Preparation of Nickel Parts by Jet Electro-Deposition Technique Based on Templates and Grinding

Gui-Feng Wang[1,*], *Zong-Jun Tian*[2], *Zhi-Dong Liu*[2], *Li-Da Shen*[2], *Jun Zhu*[2]

[1] State Key Laboratory of Coal Resources and Safe Mining, China University of Mining and Technology, No. 1 University Road, Xuzhou, Jiangsu 221116, PR China.
[2] College of Mechanical and Electrical Engineering, Nanjing University of Aeronautics and Astronautics, No. 29 Yudao Street, Nanjing, Jiangsu 210016, PR China.
[*]E-mail: wgfskl@163.com

Received: 13 May 2015 / *Accepted:* 5 June 2015 / *Published:* 24 June 2015

The synthesis of nano-crystalline nickel parts by a novel jet electro-deposition (JED) based on stacking templates layer-by-layer and real-time grinding of hard particles was investigated. Factors affecting the morphology, surface roughness and microstructure, such as deposition time and current density were discussed. Results indicated that the continuous grinding of the hard particles could remove defects, including pits or nodules, on the deposition surface and thereby greatly increased the thickness of the deposition layer. The growth effect of nodules would compete with the grinding effect of the hard particles during JED. Compared with traditional JED, the increasing trend of surface roughness with the increasing current density had been reduced obviously under the influence of the grinding effect of hard particles. When the growth rate of nodules caused by the current density balanced with the grinding effect of the hard particles, the surface of the deposit was smooth, and of the highest quality. And there was no need to take down the cathode repeatedly and conduct machining processing on the deposition surface again and again. Therefore, the prototyping process had been significantly simplified.

Keywords: jet electro-deposition; rapid prototyping; metal parts.

1. INTRODUCTION

Rapid prototyping by JED was first proposed by Bocking [1-2] in 1991. Bocking also accelerated JED by applying a laser and an increased current density for the electro-deposition of pure gold at 1,600 A/dm^2 at a rate of 16 μm/s. JED allows high current densities, high current efficiency, a refined metal structure, and compact electroformed parts [3-4]. All these advantages contribute to the formation of compact nano-crystalline deposits. However, the large current density also intensifies the propensity for defects, such as nodules or dendrites, to grow. This technology cannot be applied to produce thicker nano-crystalline metal parts. At present, without effective control measures, the thickness of metal parts prepared by JED is less than 0.5 mm [5-6]. Kunieda [7] revealed that the effective deposition zone with JED was within the area whose diameter was twice that of the nozzle, which leads to poor size and shape control of electrodeposited metal parts. So, the limited thickness and inaccuracies in size and shape of metal parts inhibit the development of rapid prototyping-oriented JED technology. Template electro-deposition is one of the procedures applied for production of new materials. For instance, anodic aluminium oxide (AAO) with lots of pores is employed as the template for production of semiconductors by the electrochemical method [8]. The most useful feature of the technology is its ability to precisely copy shape characteristics of the template in electro-deposition.

In this research, the layer-by-layer stacking of templates, and real-time grinding of hard particles, was introduced to the JED process. Thereby, the aforementioned JED problems could be overcome, thus allowing the formation of nano-crystalline metal parts. Factors affecting the morphology, surface roughness and microstructure, such as deposition time and current density were investigated.

2. EXPERIMENTAL WORK

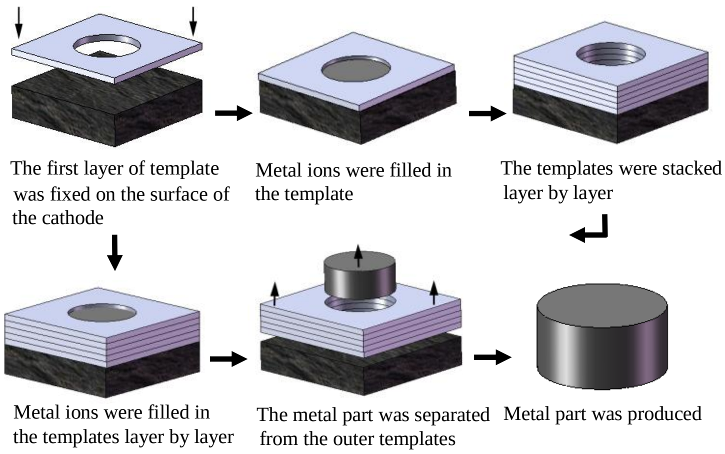

Figure 1. JED process based on the layer-by-layer stacking of templates

Fig. 1 shows the JED process based on the layer-by-layer stacking of templates. The process is summarised thus:

1) The three-dimensional (3-d) computer-aided design (CAD) model of the parts for processing is established. Then the 3-d model is sliced into layers of a certain thickness. In this way, the 3-d model is divided into several layers and the two-dimensional (2-d) outline information for each layer is obtained [8, 9].

2) After reading the information from each layer to a computer numerically controlled engraving machine, templates with the same 2-d information as the sliced layers are produced.

3) A template is fixed on the surface of the cathode. Based on JED, metal ions are filled,

layer-by-layer, in the templates, which are stacked according to the slicing sequence of the 3-d model. The continuous stacking of layers of metal depositions forms the required metal part.

The metal part is separated from the outer template.

Fig. 2 shows a schematic diagram of the JED system developed in this research. The templates were attached to the surface of the cathode substrate (cylinder with side platform) according to the slicing sequence of the 3-d model. According to processing information, JED was moved from *x* to *y* under the control of a computer, and the jetting height of the nozzle was adjusted accordingly. In this process, metal ions were deposited on the exposed area of the cathode while there was no deposition on that area covered by the template. After the nozzle had scanned the area several times, the cathode was driven into a hard particle swarm through the rotation of the rotatable platform, and swung repeatedly in the hard particle swarm. The hard particles continuously grinded and struck the surface of the cathode, and thereby effectively removed the impurities adsorbed and defects such as nodules or dendrites formed on the surface of the deposition layer. By setting the ratio of the duration of JED to the duration of the swinging-grinding operation, we researched the relationship between the electro-deposition rate of JED and the quality of the deposit produced with the grinding of hard particles. In the technology, the grinding and struck power of hard particles on the surface of the cathode arose from the movement of the rotatable platform and the vibration of the recovery tank.

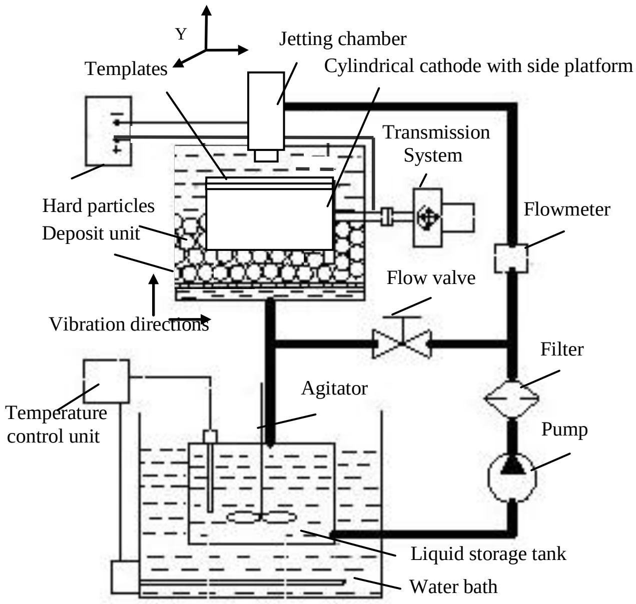

Figure 2. Schematic diagram of JED system based on templates and grinding

Ceramic balls of 1 to 2 mm in diameter were used as the hard particles and a graphite plate was adopted as the cathode. The compositions of the electrolyte were as follows: 280 g·L^{-1} of $NiSO_4 \cdot 6H_2O$, 40 g·L^{-1} of $NiCl_2 \cdot 6H_2O$, 38 g·L^{-1} of boric acid, and 2 g·L^{-1} of saccharin. The pH of the electrolyte was adjusted to 3.8 to 4.3 and the temperature was 50 °C. All reagents were analytically pure.

The micro-hardness of the nickel deposits was tested using an HXS-1000A digital intelligent micro-hardness tester. Corrosion resistance tests were conducted in a beaker. NaCl with a concentration of 3.5% was applied as the corrosion-inducing medium. All specimens were analysed either two, or three, times.

3. RESULTS AND DISCUSSION

Fig. 3 shows surface profiles of the nickel deposits produced at different times by traditional JED and the JED based on grinding. As shown in Fig. 3a and b, after electro-deposition for 60 min, numerous nodules appeared on the surface of the nickel deposits during traditional JED. As the electro-deposition continued, the nodules develop faster and larger. Meanwhile, many big protrusions appeared and developed in Fig. 3a and b, which would rapidly grow into dendrites as deposition time prolonging. In this case, it is very difficult to continue the electro-deposition. But in Fig. 3c and d, by adding the hard particles, the nodules on the deposition surface were grinded violently. The deposition surface was smooth and compact, which differed significantly from that displayed in Fig. 3a and b. While as electro-deposition continued, the surface of the nickel deposit smoothed continuously with a better surface quality. This indicated that the hard particles had grinded and struck the surface of the deposition surface and thereby influenced the growth of the deposit. Furthermore, the grinding effect would become more significant with increased electro-deposition time. Therefore, the electro-deposition was realised in a continuously repeated cycle of the two processes of particle grinding and metal ion crystallisation on the deposition surface after the nodules on the surface were rubbed off. The existence of scratches on the deposition surface proves the polishing effect of free particles during JED based on grinding.

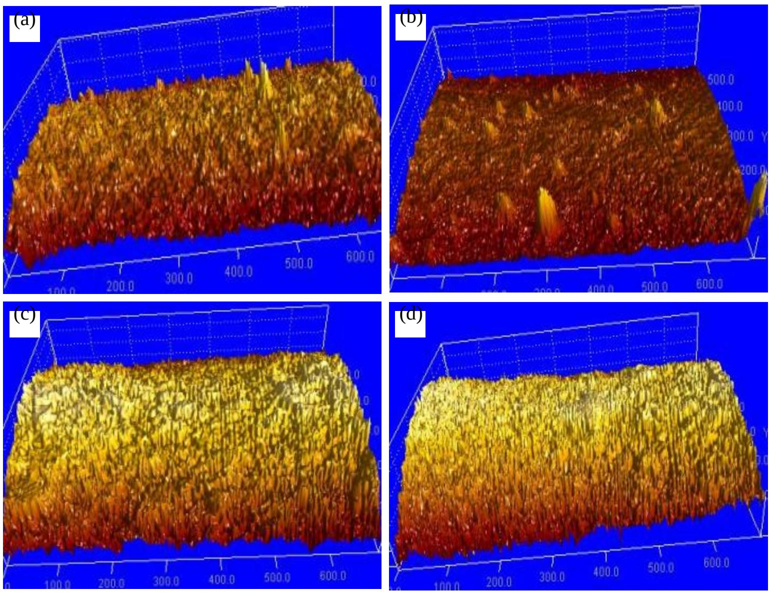

Figure 3. Surface profiles of the nickel deposits produced at different times of (a) 100 min, (b) 120 min by the traditional JED, and at different times of (c) 100 min, (d) 120 min by the JED based on grinding.

Fig. 4 shows the SEM morphologies of the nickel deposits produced by traditional JED and the JED based on grinding. These indicated that the hard particles induced a significant grinding effect. In Fig. 4(b), the cellular nodules were worn completely and a smooth surface composed of numerous small planes and band-like appeared. Similar results were obtained in the electro-deposition carried out by Weil *et al* [10] and Zhu *et al* [11-12]. Fig. 5 shows the variation of surface roughness of deposits electro-deposited at different times by traditional JED and the JED based on grinding. Due to the grinding of the hard particles, the roughness of the surface fluctuated slightly compared with that of the deposits produced by traditional JED.

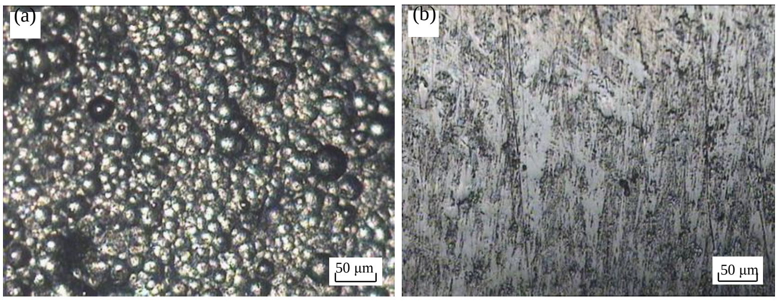

Figure 4. SEM morphologies of deposits electro-deposited by traditional JED (a) and the JED based on grinding (b).

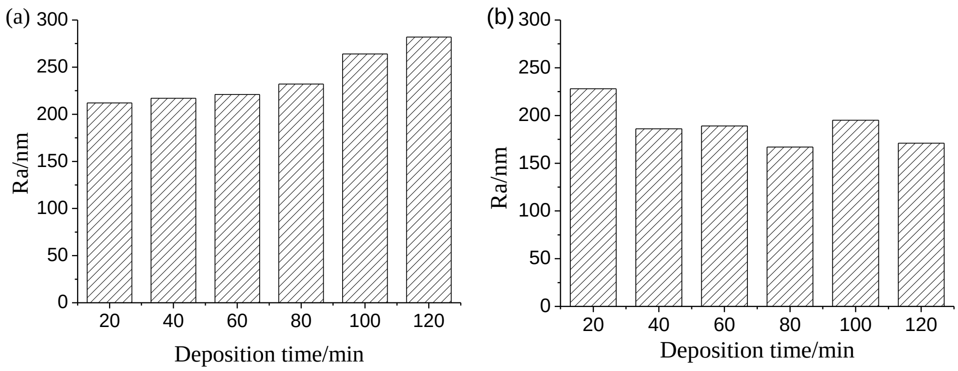

Figure 5. Variation of surface roughness of deposits produced at different times by traditional JED (a) and the JED based on grinding (b)

The surface profiles of the nickel deposit produced at different current densities by traditional JED is shown in Fig. 6. At low current densities, there were some slightly cellular nodules and a smooth deposition surface. As the current density increased, numerous cellular nodules of different sizes were formed on the deposition surface and they grew faster. The difference between the nodules kept increasing and there were large gaps and holes found between the nodules. And the roughness of the deposited surface increased significantly as shown in Fig. 9a. Additionally, the nodules would grow constantly during electro-deposition, during which large nodules collided and covered the smaller ones. As a result, there were numerous holes would form between these large nodules, which reduced the compactness of the deposit [13-15]. Therefore, it is very important to eliminate or inhibit the fast growth of nodules on the deposition surface during JED.

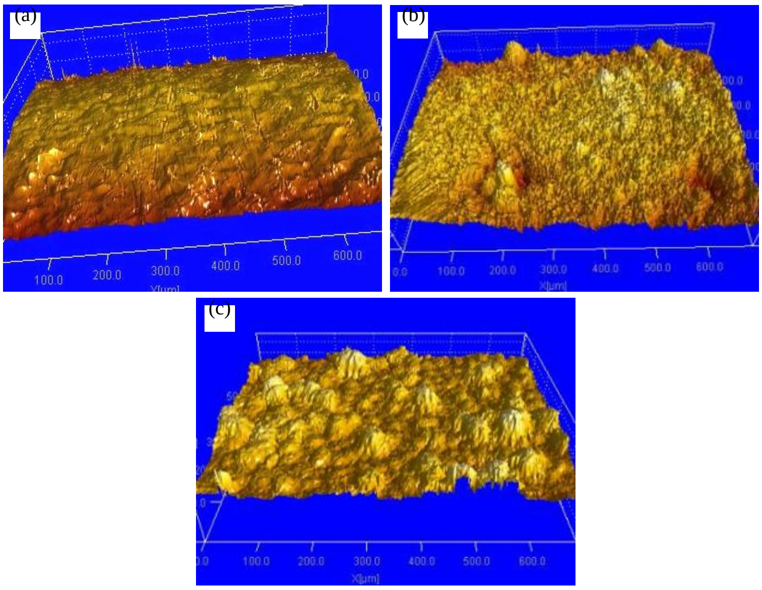

Figure 6. Surface profiles of nickel deposits prepared at different current densities of (a) 40 A/dm^2, (b) 80 A/dm^2, (c) 120 A/dm^2 by traditional JED

Fig. 7 shows the metal parts produced by traditional electro-deposition with the stacking of templates. Influenced by the point discharge effect and impurities, defects such as nodules or dendrites were formed frequently on the deposition surface and the boundary of the templates, and became more prevalent in the electro-deposition process. So, the electro-deposition had to be stopped regularly to remove the nodules or dendrites on the surface by a machining process [16]. The electro-deposition was then continued once again after the mechanical grinding of deposition surface. The technique showed low efficiency, complexity in its operation, a long production period, and an even-layered deposit of reduced quality due to the machining process.

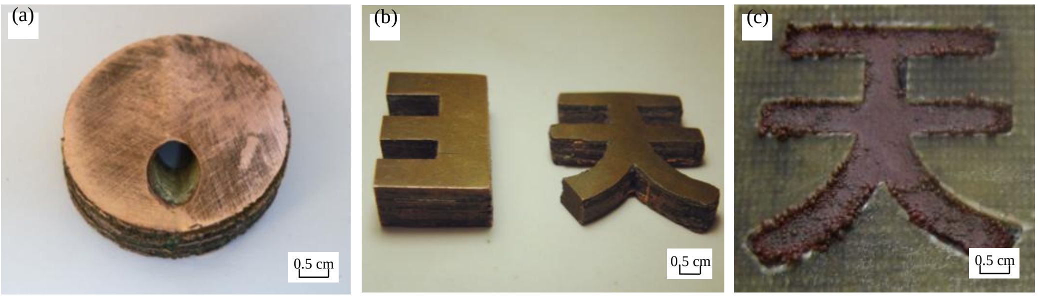

Figure 7. Metal parts produced by traditional electro-deposition with the stacking of templates

Fig. 8 shows the surface profiles of nickel deposits produced at different current densities by JED based on grinding. It indicated that with a current density of 40 A/dm^2, scratches were observed on the deposition surface. This was because, with the low current density, only a few metal ions electrodeposited on the substrate at the beginning of the JED process and the grinding of the hard particles damaged the deposition surface to some extent. As the current density increased, more metal ions were deposited, and the nodules grew more quickly on the deposition surface. The growth effect of nodules would compete with the grinding effect of the hard particles. Therefore, the smoothness of the deposition surface was improved. At a current density of 80 A/dm^2, the growth rate of the nodules and the grinding effect of the hard particles balanced and the surface was smoother. Afterwards, with the increase of current density, metal ions were consumed more quickly, which caused the increase of concentration polarisation on the surface of the cathode. The diffusion was dominant in JED and the growth effect of nodules increases greatly. Consequently, the nodules on the surface of the cathode grew both faster, and larger, on the deposition surface. The grinding effect of the hard particles could not significantly inhibit the growth of the nodules. As shown in Fig. 8(c), as the current density increased to 120 A/dm^2, the deposition surface became rougher obviously. The morphology changes indicated that current density could effectively affect the surface morphology of the deposit. Moreover, when the growth rate of nodules caused by the current density balanced with the grinding effect of the hard particles, the surface of the nickel deposit was smooth, and of the highest quality. Fig. 9 shows the variation of surface roughness of deposits produced at different current densities by JED based on grinding. As shown in Fig. 9b, the increasing trend of surface roughness with the increasing current density had been reduced obviously under the influence of the grinding effect of hard particles.

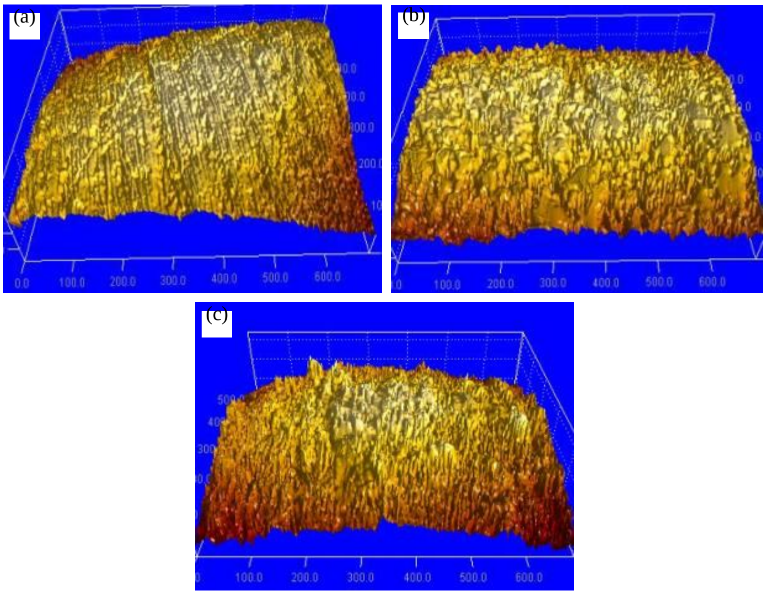

Figure 8. Surface profiles of nickel deposits prepared at different current densities of (a) 40 A/dm^2, (b) 80 A/dm^2, (c) 120 A/dm^2 by JED based on grinding.

Fig. 10 shows the TEM morphologies of the nickel deposits produced by traditional JED and the JED based on grinding. It revealed that crystal grains were distributed non-uniformly in the deposit produced by traditional JED. There were small crystal grains among the large ones and the size of some crystal grains reached 110 nm. While, the crystal grains of the deposit produced during grinding

JED were distributed uniformly, and without defects (including neither twinned crystals nor dislocations).

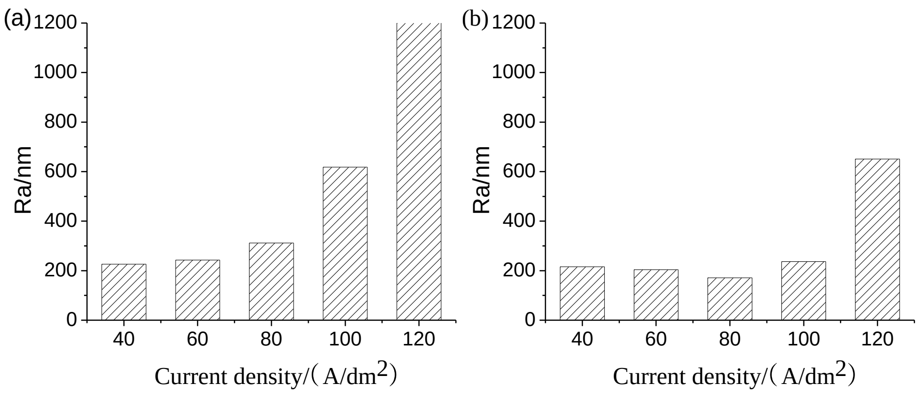

Figure 9. Variation of surface roughness of deposits electro-deposited at different current densities by traditional JED (a) and the JED based on grinding (b)

The crystal grains were refined and the largest grain size was 60 nm. The deposit had a compact and uniform structure. More spots were involved in diffraction and the diffraction pattern was a series of regular concentric diffraction rings which indicated that the grinding effect of the hard particle exerted significant influences on the micro-structure of the deposit in Fig. 10d. The average sizes of the crystal grains in the two deposits produced by the traditional and the JED based on grinding were 70 and 30 nm respectively.

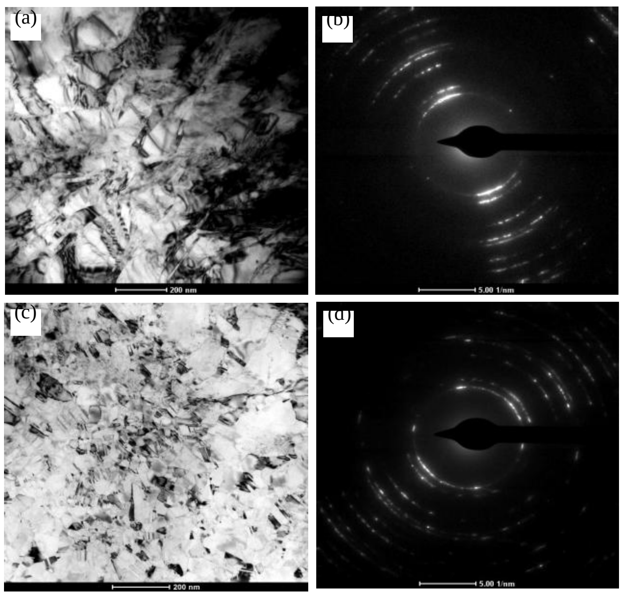

Figure 10. TEM morphologies of nickel deposits produced by traditional JED (a), (b), and the JED based on grinding (c), (d).

To test the compactness of the deposit, corrosion resistance tests were conducted in NaCl solution for the nano-crystalline nickel deposits. The morphologies of the deposits (after corrosion) produced under two different conditions are shown in Fig. 11. The morphologies were significantly different. For deposits produced by traditional JED, the many corrosion pits found on the surface had a random distribution and corrosion depth. By applying the grinding of hard particles, the amount of corrosion pits on the deposition surface was reduced and the corrosion resistance was improved. Furthermore, grinding scratches were still observed on the deposition surface after corrosion. In JED based on grinding, the hard particles continuously grinded and struck the deposition surface and therefore refined the crystals, and the nickel deposit exhibited a high grain-boundary density, which provided more active spots for the subsequent nucleation of the passive film. In this way, a more continuous, compact, passive film was formed rapidly. The passive film inhibited the participation of nickel ions or electrons in the electrochemical reaction by restraining their migration to the surface, therefore resulting in a higher corrosion resistance for the deposit [17-18].

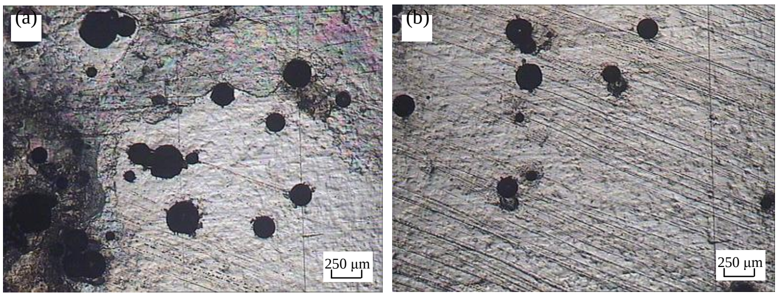

Figure 11. Morphologies of the deposits after corrosion produced by JED (a) and the JED based on grinding (b)

Fig. 12 shows a nickel part produced by JED based on templates and grinding. The part was 2.1 mm in thickness and it is enlarged in Fig. 10(b). The nickel part had the desired shape and dimensions. According to the JED technology based on templates and hard particle grinding, the grinding of the hard particles and the electro-deposition could be performed alternately. Defects such as nodules and dendrites on the deposition surface were removed by grinding with hard particles. By doing so, the thickness of metal parts in JED could be greatly increased as well as ensuring the electro-deposition quality. Meanwhile, the operation was significantly simplified so there was no need to take down the cathode from the platform repeatedly and perform secondary machining processing on the deposition surface again and again. However, burrs and nodules on the boundary of the part could still be seen in Fig. 12(b). This was because the templates were not closely attached to each other, metal ions were therefore deposited in a non-directional way as the electrolyte eroded the gaps between templates. Therefore, the selection of template material and their stacking method require further research. Fig. 13 shows the test results for surface roughness and hardness measured along the metal part’s surface, both of which show little variability, indicating a uniform structure.

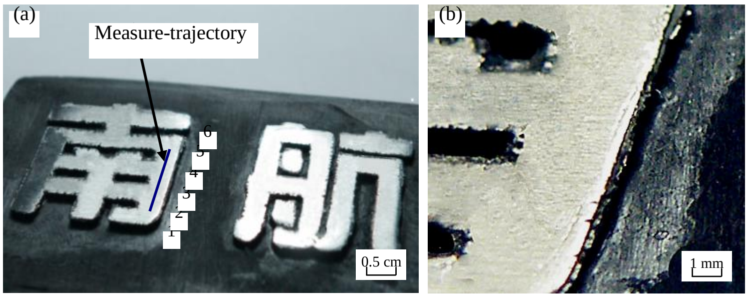

Figure 12. (a) Photo and (b) local micrograph of the nickel part produced by JED based on templates and grinding.

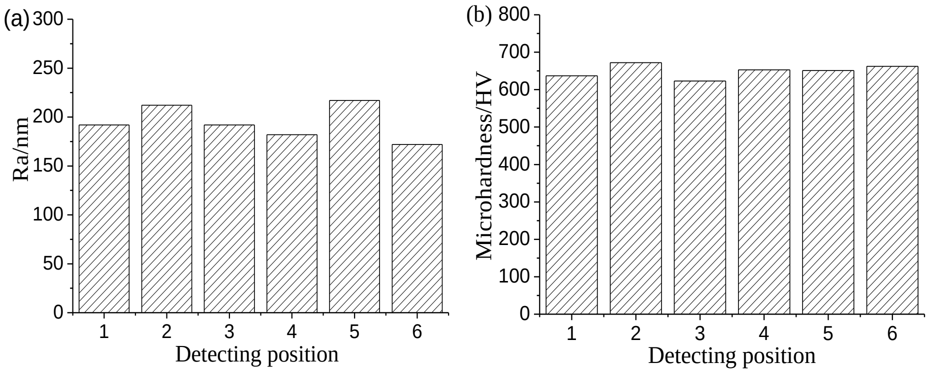

Figure 13. Distributions of (a) surface roughness and (b) micro-hardness of nickel parts

4. CONCLUSION

In JED based on templates and grinding, the polishing of hard particles and JED were carried out alternately. The continuous grinding of the hard particles could remove defects, including pits or nodules, on the deposition surface and thereby greatly increased the thickness of the deposition layer. And the growth effect of nodules would compete with the grinding effect of the hard particles during JED. Compared with traditional JED, the increasing trend of surface roughness with the increasing current density had been reduced obviously under the influence of the grinding effect of hard particles. When the growth rate of nodules caused by the current density balanced with the grinding effect of the hard particles, the surface of the deposit was smooth, and of the highest quality. And there was no need to take down the cathode repeatedly and conduct machining processing on the deposition surface again and again. Therefore, the prototyping process had been significantly simplified.

ACKNOWLEDGEMENTS

Authors acknowledge financial support from the Jiangsu Natural Science Foundation of China (Grant No. BK20140194), the Academic Program Development of Jiangsu Higher Education Institutions of China (Grant No. SZBF2011-6-B35), the Fundamental Research Funds for the Central Universities (Grant No. 2014QNB40).

References

1. C. Bocking, *Trans. Inst. Met. Finish*. 69 (1991) 119-127.
2. C. Bocking, B. Cameron, *Trans. Inst. Met. Finish*. 72 (1994) 33-40.
3. G. F. Wang, L. D. Shen, L. M. Dou, Z. J. Tian, Z. D. Liu, *Int. J. Electrochem. Sci.* 9 (2014) 220 - 226.
4. R. C. Alkire, T. J. Chen, *J. Electrochem. Soc*, 129 (1982) 2424-2432.
5. M. Karnik, A. Ghosh, R. Shekhar, *Trans. Inst. Met. Finish*. 87 (2009) 264-271.
6. D. Thiemig, J. B. Talbot, A. Bund, *J. Electrochem. Soc*. 154 (2007) 510-515.
7. M. Kunieda, R. Katoh, Y. Mori, *CIRP Ann. Manuf. Technol*. 47 (1998) 161-164.
8. E. Rocca, D. Vantelon, S. Reguer, F. Mirambet, *Mater. Chem. Phys*. 134(2012) 905-911.
9. D. H. Abbott, F. G. Arcella, *Adv. Mater. Processes*, 5 (1998) 29-30.
10. R. Weil, H. C. Cook, *J. Electrochem. Soc*, 109 (1962) 295-301.
11. Z. W. Zhu, D. Zhu, N. S. Qu, K. Wang, J. M. Yang, *Int. J. Adv. Manuf. Technol*. 39 (2008) 1164–1170.
12. Z. W. Zhu, D. Zhu, N. S. Qu, W. N. Lei, *Mater. Des.* 28 (2007) 1776–1779.
13. Y. D. Gamburg, *Elektron. Obrab. Mater.* (2003) 4-14.
14. E. Garfias-Garcia, M. Romero-Romo, M. T. Ramirez-Silva, M. Palomar-Pardave, *Int. J. Electrochem. Sci.* 7 (2012) 3102-3114.
15. S. Shivareddy, S. E. Bae, S. R. Brankovic, *Electrochem. Solid-State Lett*. 11 (2008) 13-17.
16. S. M. Silaimani, S. John, *Bull. Electrochem*. 17 (2001) 553-560.
17. A. Zarebidaki, H. Mahmoudikohani, M. Aboutalebi, *J. Alloy. Compd.* 615 (2014) 825–830.
18. A. M. Pillai, A. Rajendra, A. K. Sharma, *Trans. Inst. Met. Finish.* 90 (2012), 44-51.