Int. J. Electrochem. Sci., 15 **(2020)** 2851 – 2862, doi: 10.20964/2020.04.12

International Journal of
ELECTROCHEMICAL
SCIENCE
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Effect of Saccharose Concentration and Temperature on the Internal Stress and Corrosion Resistance of Electroplated Chromium Coatings Prepared from Chromium (III) Bath

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Received: 29 November 2019 / *Accepted:* 2 February 2020 / *Published:* 10 March 2020

The trivalent chromium carbon coatings are electroplated from different electroplating temperature (10, 0 and -5℃) and different concentration (0.01, 0.02 and 0.03 M) of saccharose ($C_{12}H_{22}O_{11}$). The saccharose play a role of stress inhibitor in the bath during electroplating process. The results of internal stress analysis show that the internal stress of the trivalent chromium carbon coating decreases with the increase of concentration of saccharose at individual electroplating temperatures, this shows that saccharose has the effect on suppressing the accumulation of stress within the coating. Moreover, the electroplating temperature also affect the internal stress of trivalent chromium carbon coatings i.e. the lower electroplating temperature (-5℃) will reduce the accumulation of stress within the coating during electroplating. The smallest internal stress of trivalent chromium carbon coatings is 13.4 MPa, electroplated at -5℃ with a concentration of saccharose at 0.02 M. The best i_{corr} is approximately at 1.32×10^{-6} A/dm^2, this coatings is also electroplated at -5℃ and the concentration of saccharose at 0.02 M. The results indicated that both electroplating temperature and concentration of saccharose can reduce the internal stress within trivalent chromium carbon coatings and decrease the through-deposit cracking within coatings, thereby improving the corrosion resistance of coatings.

Keywords: trivalent chromium carbon coatings, internal stress, electroplating temperature

1. INTRODUCTION

The conventional hexavalent chromium coatings had been banned by REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) and RoHS (Restriction of Hazardous Substances) due to the intense toxicity of Cr(VI) ions and evolution of toxic fumes during electrodeposition process. Therefore, in recent years, the trivalent chromium-carbon coatings has been

developed to substitute the hexavalent chromium due to its excellent corrosion resistance, high hardness and lower toxicity [1-5]. However, trivalent chromium or chromium-carbon coatings still has a shortcoming i.e. the accumulation of internal stress during electrodeposited process will form cracks within coatings and reduce their corrosion resistance. Huang et al. [6,7] indicated that a pre-electroplated nickel deposit on steel substrates can avoid through-deposit cracking within Cr-C coatings during electroplating. But the corrosion resistance of their Cr-C coatings were still poor [6,7]. How to reduce the internal stress of Cr-C coatings become a very important topic. In our previous studies [8,9] indicated that the Al_2O_3 particles added into Cr-C bath to prepare a Cr-C/Al_2O_3 composite coatings can reduce the internal stress of Cr-C coatings and enhance their hardness. However, it is necessary to study how to reduce the internal stress of Cr-C coatings without adding Al_2O_3 particles. Ghaziof et al. [10,11] tried to reduce the internal stress of Cr-C coatings by adjusting the plating solution and adding different additives such as potassium chloride, ammonium chloride and sodium sulfate. Unfortunately, the surface of the Cr-C coatings is still covered with cracks caused by internal stress, and the corrosion resistance is still poor. He et al. [12] used [BMIM]HSO_4 (1-butyl-3-methylimidaz olium-hydrogen sulfate) as an additive and changed different electrodeposited parameters to prepare Cr-C coating. Unfortunately, the corrosion resistance of their Cr-C coatings still did not be improved.

Therefore, in this study, we try to reduce the internal stress of Cr-C coatings by adding different concentration of saccharose into plating solution and the electroplating temperature, the corrosion resistance of Cr-C coatings are also studied.

2. EXPERIMENTAL

In this work, the trivalent chromium carbon coatings were electroplated on copper substrates with a dimension of 50 × 50 × 2 mm. The copper substrates are placed in ethanol with an ultrasonic cleaning process for 10 minutes and then cleaning using deionized water, activated by 3% NaOH solution for 60 seconds and immersed into a 15 % hydrochloric acid solution for 30 seconds before electrodeposited process. The composition of the trivalent chromium electroplating solution including 0.3 M $CrCl_3 \cdot 6H_2O$ as the main metal salt, 1 M ammonium formate as complexing agent, 0.03 M KBr, 0.5 M KCl and 0.5 M $B(OH)_3$. Different concentration of saccharose ($C_{12}H_{22}O_{11}$) such as 0.01 M, 0.02 M and 0.03 M are added into the electroplating solution. The electroplating current density and electroplating period is at 10 A/dm^2 and 15 mins that is the optimal operated parameters in our previous studies [13, 14].

The surface morphology and cross-sectional photographs of trivalent chromium carbon coatings were observed by a scanning electron microscopy (SEM, HITACHI S-3000 N, operating at 15 kV). The measurement of internal stress of trivalent chromium carbon coatings electroplated from different electroplating parameters were carried out with a deposit stress analyzer (model 683EC). The internal stress analyzer method for the judgements of the internal stress within thin films is based on a bending state of the standard test piece made by copper, and the deposited metallic thin films will cause a warping of the standard test piece, increased scale can be read from internal stress analyzer (Fig. 1). The standard test piece has a deposited surface area of 3.05 cm^2. As a thin film is deposited on the standard test piece,

the divided part of the test piece separates so as to allow to measure the increased angle in the analyzer. Formula to calculate internal stress as following:

$$S = 5.94 \times \frac{UK}{T} \text{ kgf/mm}^2 \quad (1)$$

$$T = 1.29 \times \frac{W}{D} \times 10^4 \text{ μm} \quad (2)$$

where, S = internal stress of thin films (kgf/mm^2), U = total number of increments spread, K = test strip calibration constant (kgf/mm), T = average thickness thin films (μm), W = weight of thin films (g) and D = Specific gravity of the deposited thin films (g/cm^3).

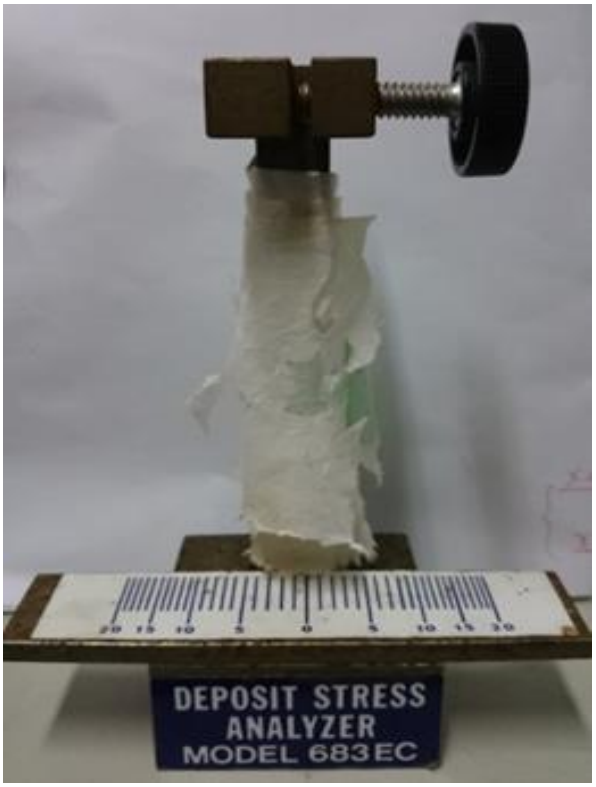

Figure 1. The test stand and scale of deposit stress analyzer: model 683EC.

The analysis of corrosion resistance of specimens were measured by an Autolab-PGSTAT30 system. The electrochemical behavior of trivalent chromium carbon deposits were analyzed using specimens soaked into a 3.5% NaCl solution at room temperature. The analyzed potential range from −0.3 V to 0.8 V. Before measurement, the lipid in surface of samples were removed by DI water.

3. RESULTS AND DISCUSSION

Fig. 2 presents the surface morphology and cross section image of trivalent chromium carbon coatings electrodeposited on copper substrates without addition of saccharose. The obvious cracks appear on the surface of the trivalent chromium carbon coating (Fig. 2a), and the through-deposit

cracking appear in trivalent chromium carbon coating (Fig. 2b). The appearance of through-deposit cracking can be attributed to the greater internal stress of trivalent chromium carbon coating during electroplating process [7], and this kind of cracks will reduce the corrosion resistance of trivalent chromium carbon coating. The potentiodynamic polarization curves of trivalent chromium carbon coating electroplating without added saccharose into the bath is shown in Fig. 3. The value of i_{corr} is also calculated and presented in Table 1, its i_{corr} is approximately at 1.25×10^{-5} A/dm^2.

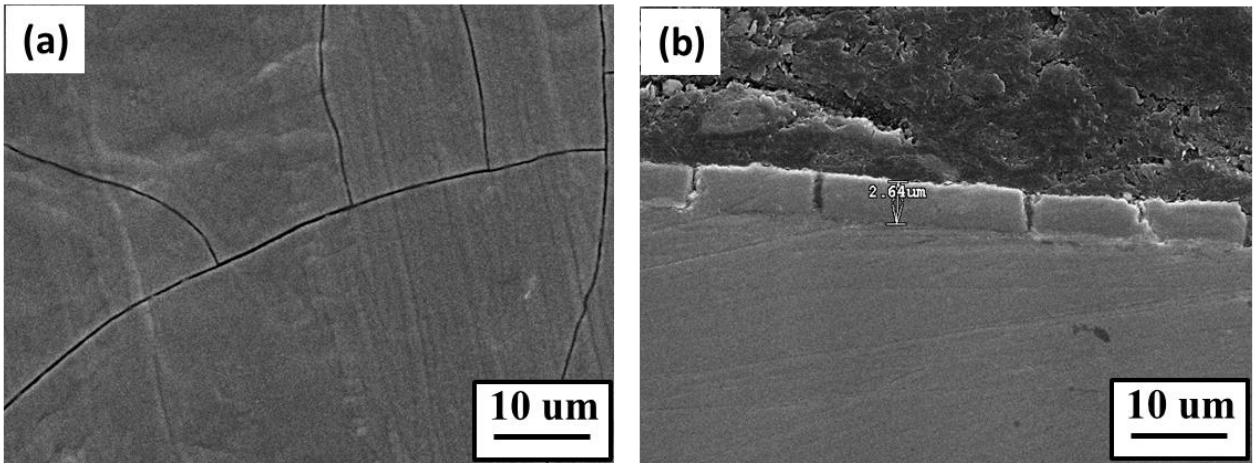

Figure 2. The SEM images of Cr-C coatings electroplated from the bath without added $C_{12}H_{22}O_{11}$ (a) morphology, (b) cross-section.

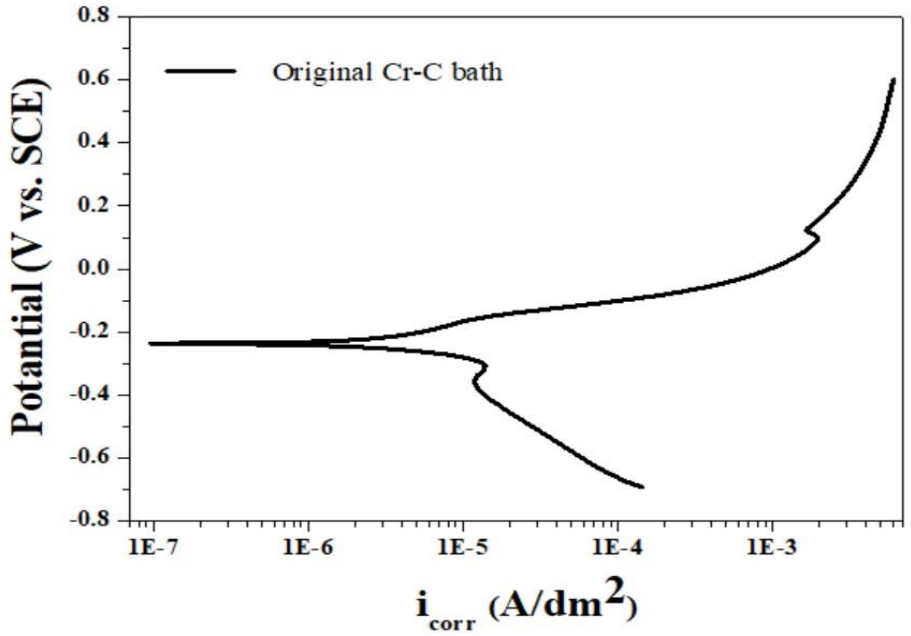

Figure 3. Polarization curves of chromium-carbon coatings electrodeposited from the bath without added saccharose ($C_{12}H_{22}O_{11}$).

In order to improve the occurrence of through-deposit cracking in trivalent chromium carbon coatings, the electroplating trivalent chromium carbon coatings are deposited from adding different content of $C_{12}H_{22}O_{11}$ and electroplating temperature, respectively. Fig. 4 shows the surface morphology and cross-sectional images of trivalent chromium carbon coatings electrodeposited at different

concentration of saccharose (0.01M to 0.03M) at 10℃. The through-deposit cracking still occurred at the electroplating condition that added 0.01 M saccharose into the bath (see Fig. 4(d)).

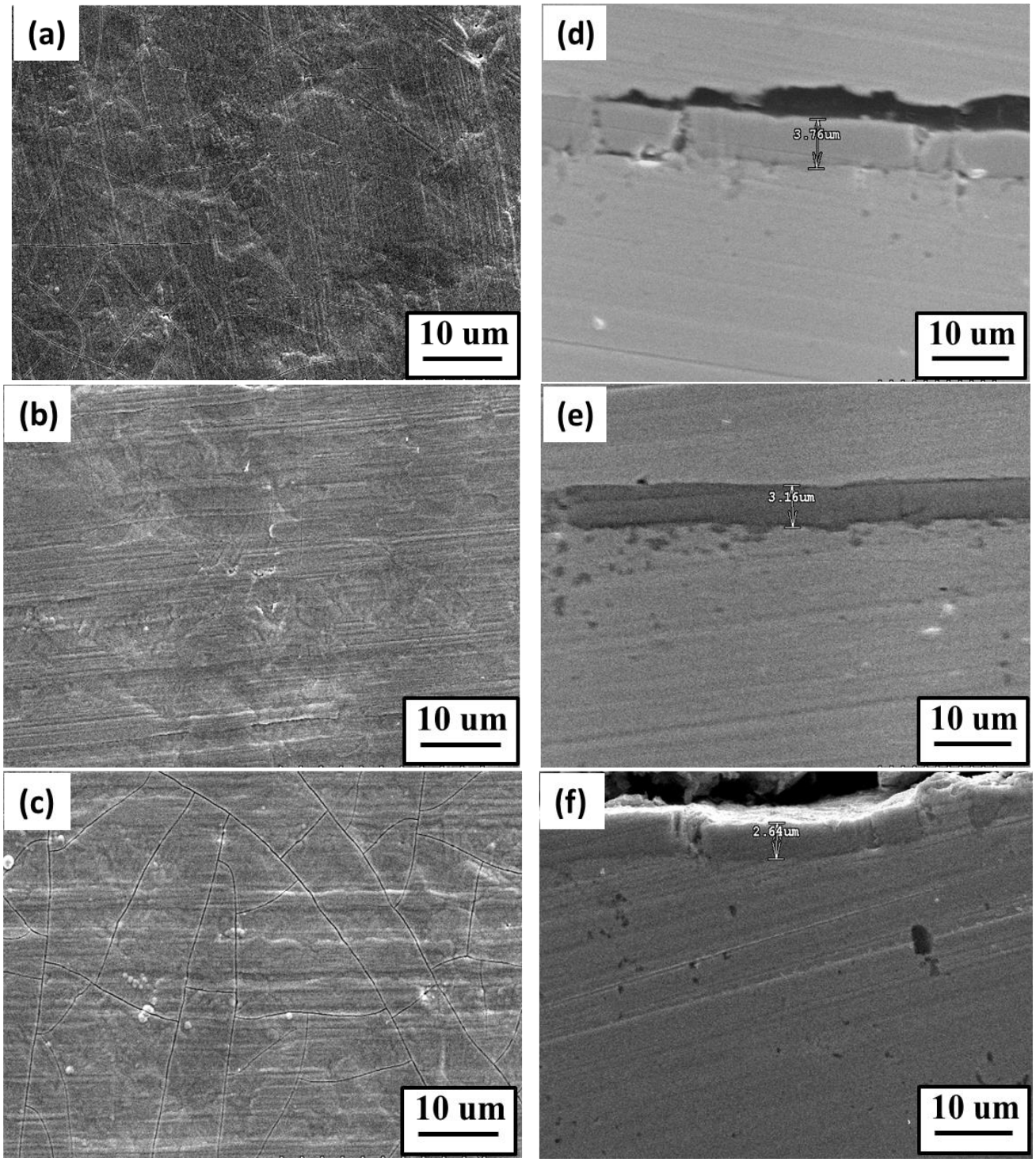

Figure 4. SEM morphologies and cross-sectional images of chromium-carbon coatings electrodeposited on substrates at 10℃ : (a)(d) added 0.01 M saccharose, (b)(e) added 0.02 M saccharose, (c)(f) added 0.03 M saccharose.

When the concentration of saccharose increase to 0.02 M, the surface cracks in the coatings disappear (Fig. 4(b)), and the through-deposit cracking also disappear in the cross section image of trivalent chromium carbon coatings (Fig. 4(e)). However, the surface cracks appear again when the concentration of saccharose increase to 0.03 M (Fig.4 (c)), the through-deposit cracking also appear again in the trivalent chromium carbon coatings (Fig.4 (f)).

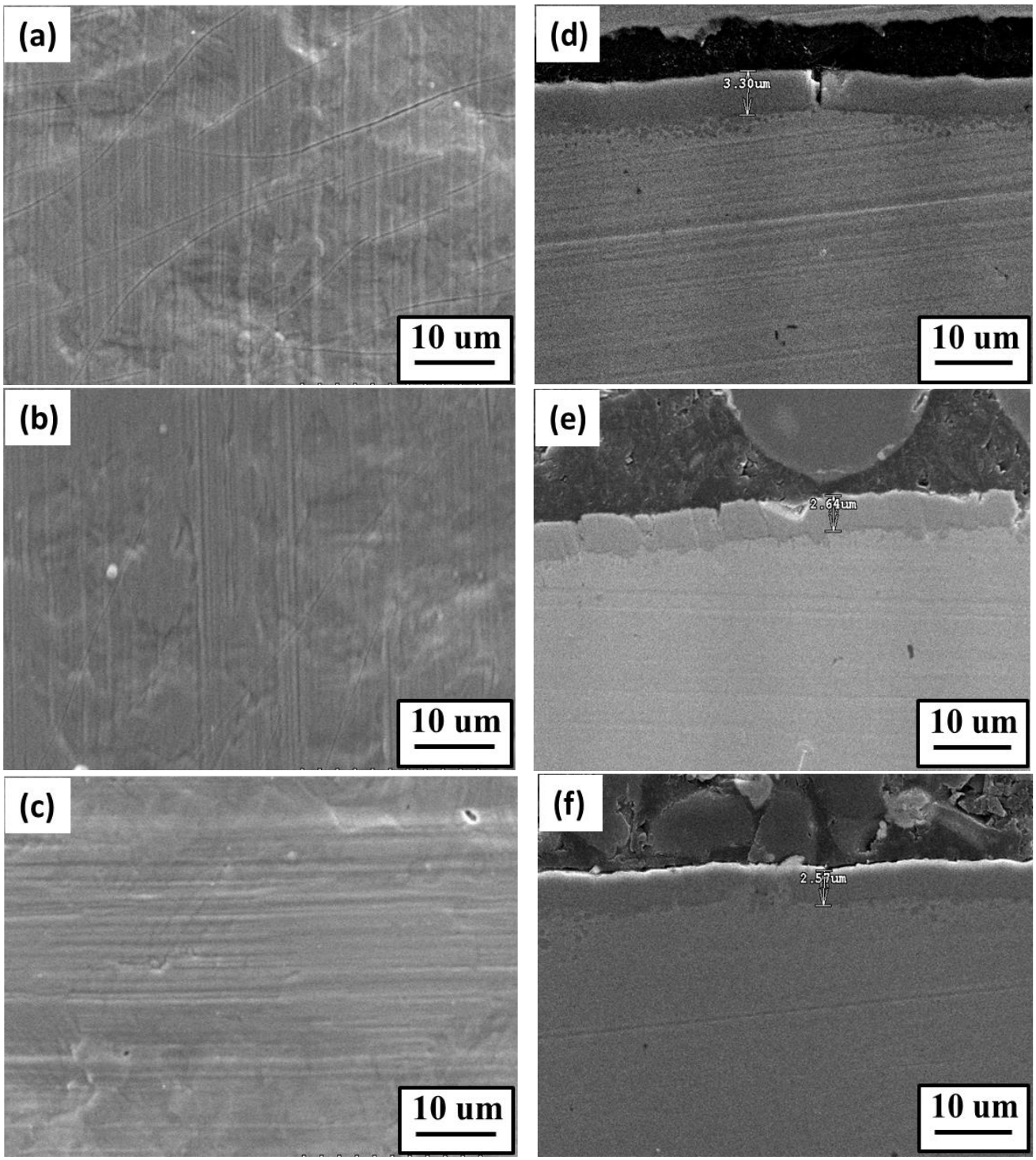

Figure 5. SEM morphologies and cross-sectional images of chromium-carbon coatings electrodeposited on substrates at 0℃ : (a)(d) added 0.01 M saccharose, (b)(e) added 0.02 M saccharose, (c)(f) added 0.03 M saccharose.

The thickness of trivalent chromium carbon coatings electroplated with different concentration of $C_{12}H_{22}O_{11}$ at 10℃ is 3.76, 3.16 and 2.64 um, respectively. Fig. 5(a)(b)(c) show the surface morphology of trivalent chromium carbon coatings electrodeposited at different added concentration of saccharose (0.01M to 0.03M) at 0℃.

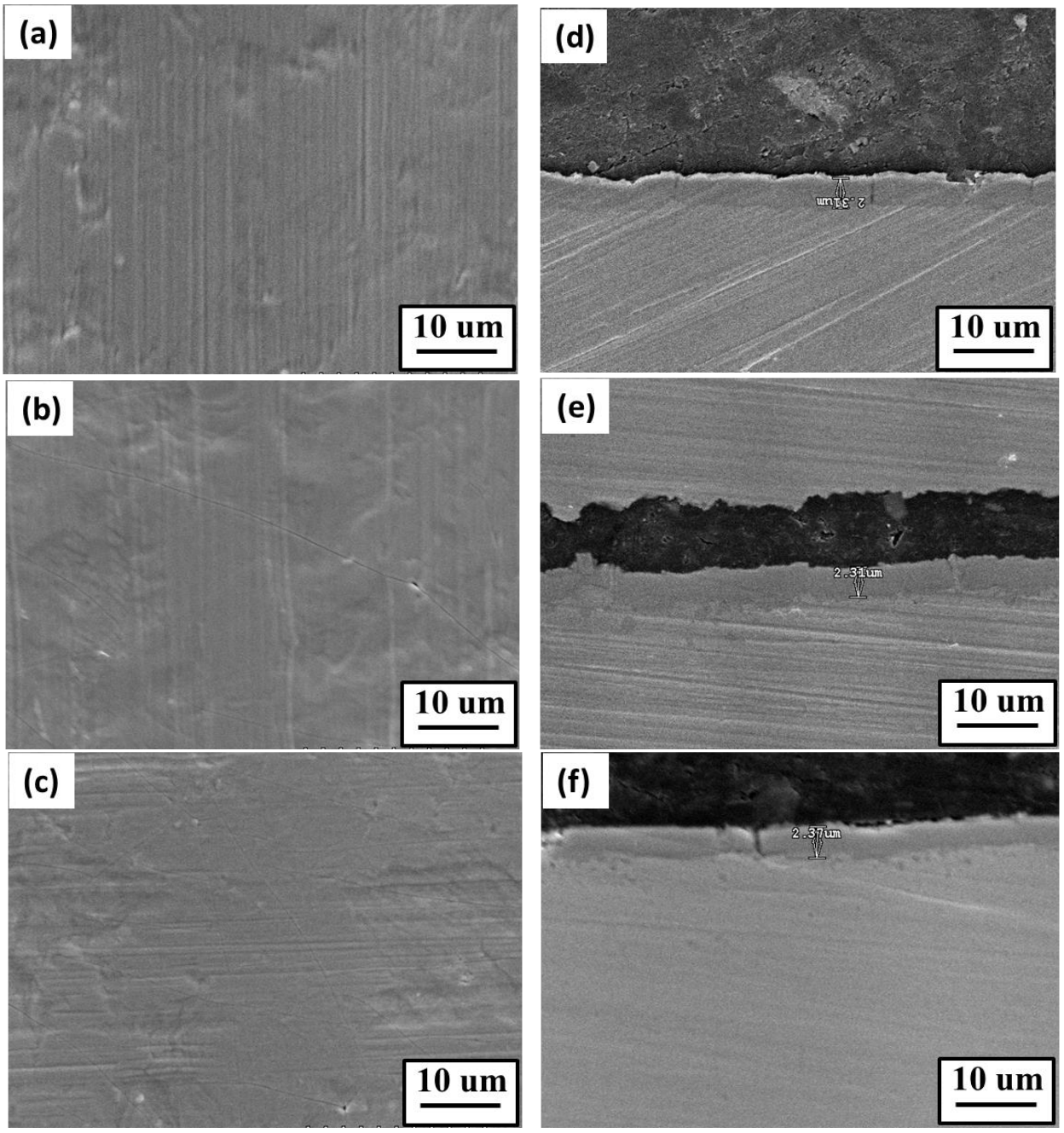

Figure 6. SEM morphologies and cross-sectional images of chromium-carbon coatings electrodeposited on substrates at -5℃ : (a)(d) added 0.01 M saccharose, (b)(e) added 0.02 M saccharose, (c)(f) added 0.03 M saccharose.

The amount of cracks in the surface morphology decrease with an increase of concentration of saccharose in the bath. The amount of through-deposit cracking also decrease with the increase of

concentration of saccharose (Fig. 5(d)(e)(f)). The thickness of trivalent chromium carbon coatings electroplated with different concentration of saccharose at 0℃ is 3.30, 2.64 and 2.57 um, respectively.

Fig. 6(a)(b)(c) show the surface morphology of trivalent chromium carbon coatings electrodeposited at different concentration of saccharose (0.01M to 0.03M) at -5℃. The amount of cracks in the surface morphology electroplated at -5℃ significantly reduce than that of trivalent chromium carbon coatings electroplated at 0℃ and 10℃. In electroplated temperature at -5℃, the amount of through-deposit cracking in the coatings electroplated from added 0.03 M saccharose is greater than that of coatings electroplated from added 0.01 M and 0.02 M saccharose (see Fig. 6(d)(e)(f)). The thickness of trivalent chromium carbon coatings electroplated with different concentration of saccharose at -5℃ is 2.31, 2.31 and 2.37 um, respectively.

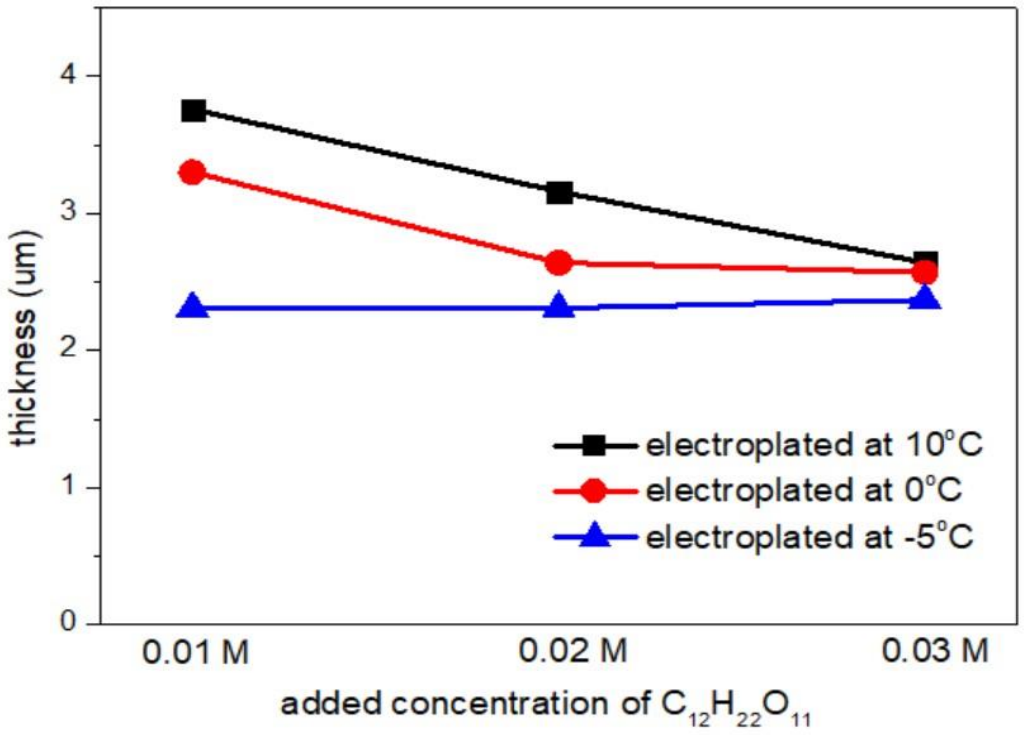

Figure 7. The thickness of trivalent chromium carbon coatings electroplated from both different temperature and added concentration of $C_{12}H_{22}O_{11}$.

The thickness of trivalent chromium carbon coatings electroplated from both different temperature and concentration of saccharose are shown in Fig. 7. When the electroplated temperature at 10℃ and 0℃, all the thickness of trivalent chromium carbon coatings decrease with an increase of concentration of saccharose, the results indicated that the greater concentration of saccharose will inhibit the deposition rate of trivalent chromium carbon coatings. The results is agreement with the study of Wang et al. [15] that added saccharin ($C_7H_5NO_3S$) will reduce the deposition rate of Ni-W-P alloy coatings. The addition of sodium saccharin in the bath also can reduce the deposited rate in electroplating Co-Fe magnetic film [16]. However, when the electroplated temperature at -5℃, the thickness of the trivalent chromium-carbon coating remains almost the same. In this condition, the concentration of

saccharose will not affect the deposited rate of coatings, and the electroplated temperature will play a dominate role on the deposited rate of coatings.

The measurement of internal stress of chromium carbon coatings electrodeposited at different electroplating parameters is shown in Fig. 8. The internal stress of the chromium carbon coatings electroplated from original bath (without adding saccharose) is approximately at 17.8 MPa. The chromium carbon coatings electrodeposited from different concentration of saccharose (0.01, 0.02 and 0.03 M) at 10℃ is 16.4, 16.9 and 17.0 MPa, respectively.

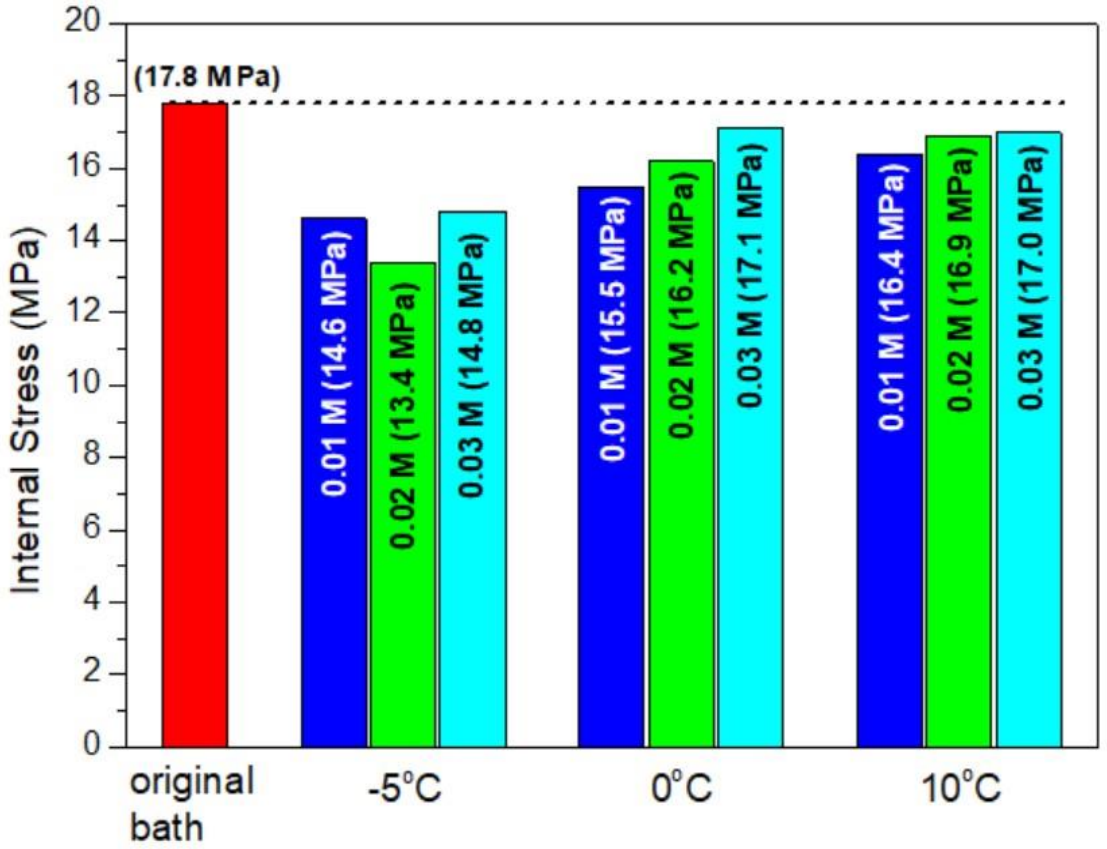

Figure 8. The measurement of internal stress of chromium carbon coatings electrodeposited at different electroplating parameters.

The chromium carbon coatings electrodeposited from different concentration of saccharose (0.01, 0.02 and 0.03 M) at 0℃ is 15.5, 16.2 and 17.1 MPa, respectively. When the electroplating temperature at 10℃ and 0℃, the internal stress of coatings increase with the increase of concentration of saccharose, and all the internal stress of coatings are lower than that electroplated from original bath. However, when the electroplating temperature at -5℃, the lowest internal stress of coatings is approximately at 13.4 MPa which occurred at the concentration of saccharose at 0.02 M. All the coatings with lower internal stress occurred at the electroplating temperature at -5℃, this can be attributed to the lower deposited rate of coatings at -5℃ will reduce the internal stress of coatings. Li et al. [17] indicated that the addition of saccharin can decrease the tensile stress of nickel deposits and result in the compressive stress eventually and reduce the internal stress of coatings during electroplating. Moreover,

the addition agent such as saccharin can inhibit the deposit rate of coatings also play a dominate role on reducing internal stress of coatings during electroplating [15, 18]. In this study, the added saccharose had the same effect as saccharin.

Fig. 9 shows the polarization curves of trivalent chromium carbon coatings electroplated from different electroplating temperature and different concentration of saccharose. Fig. 9(a) reveals the polarization curves of coatings electroplated at various electroplating temperature in the bath added 0.01 M saccharose, the best i_{corr} value is approximately at 1.76×10^{-6} A/dm^2 occurred at electroplating temperature at -5℃ (see Table 1), the worst i_{corr} value occurred at electroplating temperature at 10℃ is approximately at 5.08×10^{-6} A/dm^2. Fig. 9(b) shows the polarization curves of coatings electroplated at various electroplating temperature in the bath added 0.02 M saccharose, the best i_{corr} value is approximately at 1.32×10^{-6} A/dm^2 occurred at electroplating temperature at -5℃ (see Table 1), the worst i_{corr} value occurred at electroplating temperature at 10℃ is approximately at 8.86×10^{-6} A/dm^2.

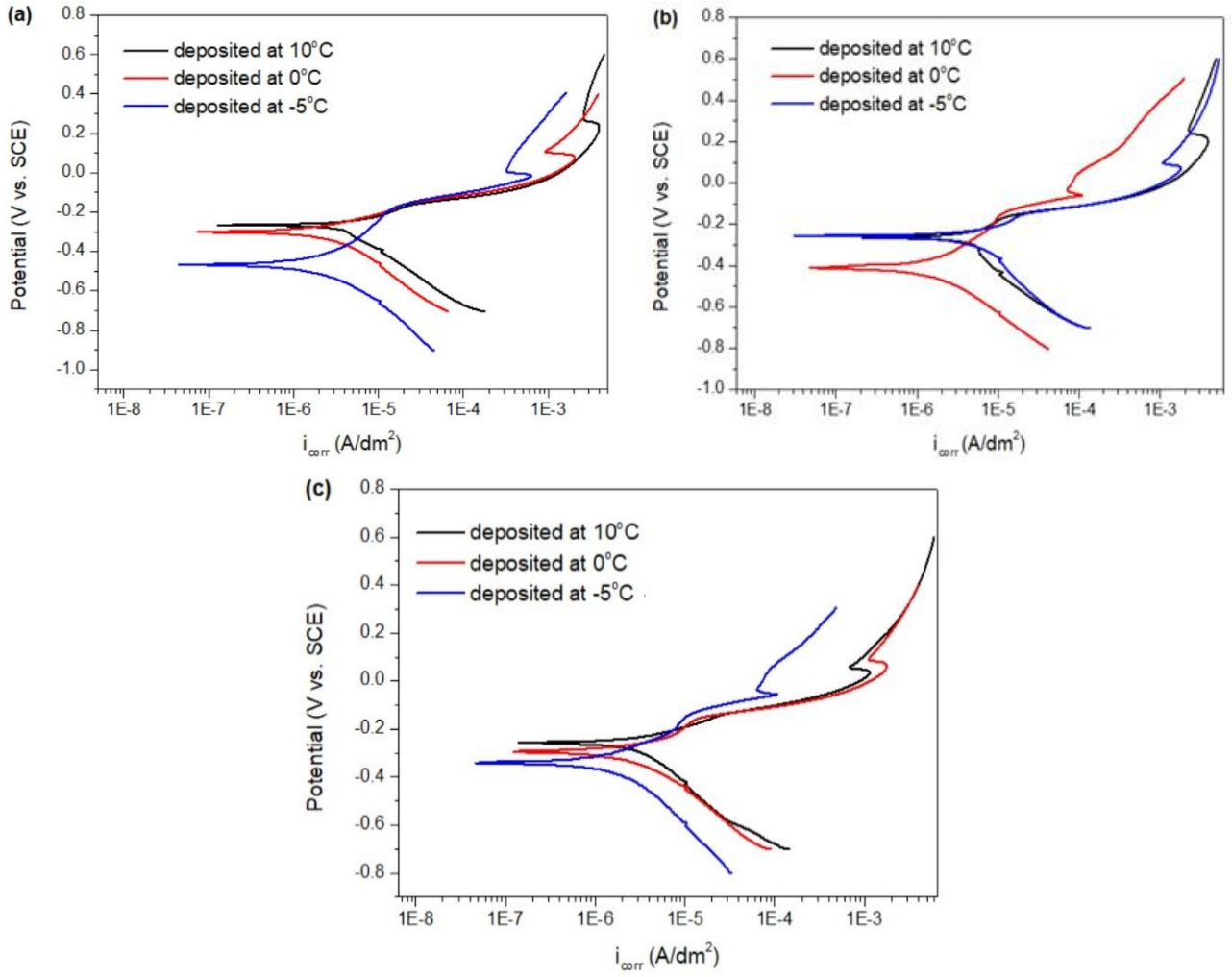

Figure 9. Polarization curves of chromium-carbon coatings electrodeposited at different electroplating temperature (10℃, 0℃ and -5℃) and different added concentration of saccharose: (a) added 0.01 M saccharose, (b) added 0.02 M saccharose, (c) added 0.03 M saccharose.

Fig. 9(c) presents the polarization curves of coatings electroplated at various electroplating temperature in the bath added 0.03 M saccharose, the best i_{corr} value is approximately at 1.82×10^{-6} A/dm^2 occurred at electroplating temperature at -5℃ (see Table 1), the worst i_{corr} value occurred at electroplating temperature at 10℃ is approximately at 9.82×10^{-6} A/dm^2. All the better corrosion resistance of trivalent chromium carbon coatings occurred at the electroplating temperature at -5℃, and their polarization curves are shown in Fig. 10. The better corrosion resistance of coatings electroplated at -5℃ can be attributed to the lower internal stress within coatings and reduce the through-deposit cracking appear within coatings.

Table 1. Corrosion resistance of trivalent chromium carbon coatings electroplated from both different temperature and concentration of saccharose analyzed from 3.5 wt.% NaCl solution.

Sample code	I_{corr} (A/dm^2)	E_{corr} (V vs. SEC)
original bath	1.25×10^{-5}	-0.23
0.01M/10℃	5.08×10^{-6}	-0.27
0.01M/0℃	3.65×10^{-6}	-0.31
0.01M/-5℃	1.76×10^{-6}	-0.47
0.02M/10℃	8.86×10^{-6}	-0.27
0.02M/0℃	4.48×10^{-6}	-0.41
0.02M/-5℃	1.32×10^{-6}	-0.25
0.03M/10℃	9.82×10^{-6}	-0.25
0.03M/0℃	5.04×10^{-6}	-0.29
0.03M/-5℃	1.82×10^{-6}	-0.34

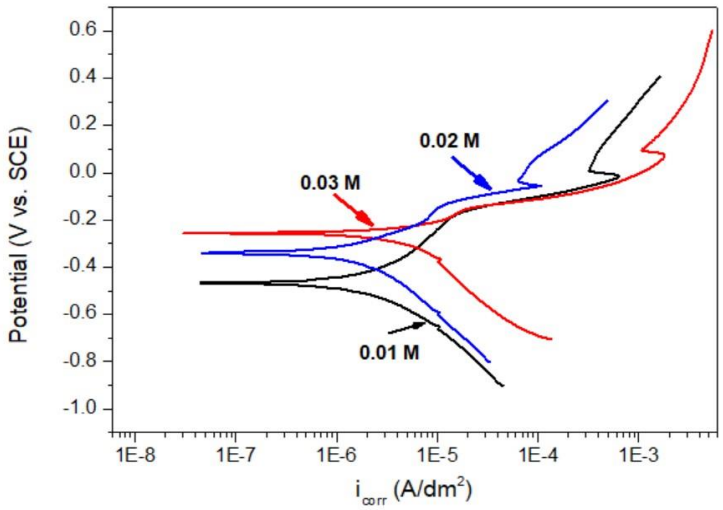

Figure 10. Polarization curves of chromium-carbon coatings electrodeposited at -5℃ with different concentration of saccharose.

4. CONCLUSIONS

The effects of electroplating temperature and concentration of saccharose on the internal stress and corrosion resistance of trivalent chromium carbon coatings were investigated. The internal stress of

coatings reduce with the decrease of electroplating temperature, the optimal electroplating temperature is -5℃. The added different concentration of saccharose into the bath also can reduce the internal stress of trivalent chromium carbon coatings, the best added concentration of saccharose is 0.02 M. The smallest internal stress of trivalent chromium carbon coatings is approximately at 13.4 MPa electroplated at -5℃ and the concentration of saccharose at 0.02 M. The best i_{corr} is approximately at 1.32×10^{-6} A/dm^2, this coatings is also electroplated at -5℃ and the concentration of saccharose at 0.02 M. The best corrosion resistance and smallest internal stress of the trivalent chromium carbon coatings is electroplated from the optimal electroplating parameters that is the electroplating temperature at -5℃ and the concentration of saccharose at 0.02 M.

ACKNOWLEDGEMENTS
The authors would like to thank the Ministry of Science and Technology of the Republic of China, Taiwan, for financially supporting this research under Contract No. MOST 104-2622-E-606-002-CC2.

References

1. V.A. Safonov, L.N. Vykhodtseva, Y.M. Polukarov, O.V. Safonova, G. Smolentsev, M. Sikora, S.G. Eeckhout, P. Glatzel, *J. Phys. Chem*. B, 110 (2006) 23192.
2. C. Quan, Y. He, *Surf. Coat. Technol.,* 269 (2015) 319.
3. J.H.O.J. Wijenberg, M. Steegh, M.P. Aarnts, K.R. Lammers, *J.M.C. Mol, Electrochim. Acta,* 173 (2015) 819.
4. H. H. Sheu, C. H. Lin, S. Y. Jian, H. B. Lee, B. R. Yang, M. D. Ger, *Int. J. Electrochem. Sci*., 11 (2016) 7099.
5. F. I. Danilov, V. S. Protsenko, V. O. Gordiienko, S. C. Kwon, J. Y. Lee, M. Kim, *Appl. Surf. Sci*., 257 (2011) 8048.
6. C. A. Huang , C. K. Lin, C. Y. Chen, *Surf. Coat. Technol*., 203 (2009) 3686.
7. C. A. Huang, U. W. Lieu, C. H. Chuang, *Surf. Coat. Technol*., 203 (2009) 2921.
8. H.H. Sheu, M.H. Lin, S.Y. Jian, T.Y. Hong, K.H. Hou, M.D. Ger, *Surf. Coat. Technol*., 350 (2018) 1036.
9. H.H. Sheu, T.Y. Hong, T.T. Lin, M.D. Ger, *Int. J. Electrochem. Sci*., 13 (2018) 9399.
10. S. Ghaziof, K. Raeissi, M.A. Golozar, *Surf. Coat. Technol*., 205 (2010) 2174.
11. S. Ghaziof, M.A. Golozar, K. Raeissi, *J. Alloy. Comp*, 496 (2010) 164.
12. X. He, Q. Zhu, B. Hou, C. Li, Y. Jiang, C. Zhang, L. Wu, *Surf. Coat. Technol*., 262 (2015) 148.
13. C.E. Lu, N.W. Pu, K.H. Hou, C.C. Tseng, M.D. Ger, *Appl. Surf. Sci*., 282 (2013) 544.
14. H.H. Sheu, J.H. Syu, Y.M. Liu, K.H. Hou, M.D. Ger, *Int. J. Electrochem. Sci*., 13 (2018) 3267.
15. Y.H. Wang, M.Q. Yu, H.L. Luo, Q. Qiao, Z. Xiao, Y. Zhao, L. Zhao, H. Sun, Z.F. Xu, K.H. Matsugi, J.K. Yu, *Journal of Materials Engineering and Performance*, 25 (2016) 4402.
16. L. Ricq, F. Lallemand, M. P. Gigandet, J. Pagetti, *Surf. Coat. Technol*., 138 (2001) 278.
17. Y.W. Li, J.H. Yao, X. Huang, *Int. J. Metall. Mater. Eng.*, 2 (2016) 123.
18. A.M. Rashidi, A. Amadeh, *Surf. Coat. Technol*., 204 (2009) 353.