Crevice Corrosion Behaviors Between CFRP and Stainless Steel 316L for Automotive Applications

Xia-Yu Wu¹ · Jia-Kun Sun¹ · Jia-Ming Wang¹ · Yi-Ming Jiang¹ · Jin Li¹

Received: 21 December 2018 / Revised: 25 March 2019 / Published online: 26 April 2019
© The Chinese Society for Metals (CSM) and Springer-Verlag GmbH Germany, part of Springer Nature 2019

Abstract

Carbon fiber reinforced plastics (CFRP) are promising lightweight materials for vehicle applications. 316L is one of the most widely used types of austenite stainless steels and applied in lots of automotive applications. The existence of crevices will result in galvanic corrosion and crevice corrosion when CFRPs and 316L are directly connected. A crevice former for the galvanic system was therefore designed and applied to evaluate the crevice corrosion behaviors and study the mechanism of galvanic crevice corrosion through several electrochemical techniques in this research. The results showed that the crevice corrosion of galvanic systems grew from crevice mouth to the inside crevice and could be divided into four steps, metastable pitting corrosion at the crevice mouth, initiating step of crevice corrosion, propagating step and ending step of crevice corrosion. Because of the influences of the galvanic system, electrode reaction rates were speeded up and the passivation region was shortened at the initiating stage of crevice corrosion. Corrosion rate was observed to be higher in the galvanic system than that in normal crevice systems.

Keywords Crevice corrosion · Galvanic system · Carbon fiber reinforced plastics · 316L stainless steels

1 Introduction

To meet the ever increasing demands, facing the trend of environment protection is one of the most important challenges in the automotive industry nowadays [1]. The researchers primarily pay attention to design concepts and the replacement of conventional materials by those of sufficient strength, lower density and good corrosion durability [2, 3]. Besides, materials such as carbon fiber reinforced plastics (CFRP) are very promising candidates for new design strategies due to their specific mechanical properties [2, 4, 5]. Because of stainless steels' satisfactory mechanical properties and corrosion resistance, stainless steel plates could be fabricated to be thinner than carbon steels and used as alternative body material for vehicles [6]. To use stainless steels as the alternative for aluminum alloys has become a new trend for the latest products of joint venture companies

to compete with the imported vehicles in the Chinese market. It not only lowers the cost of manufacturing, but also enhances the body strength of the vehicles.

However, potential material failures that attribute to corrosion, which is caused by applications of different varieties of materials, alloys and CFRPs in the manufacturing process still endanger the security and lifespan of vehicles. According to present researches, the most vulnerable part of the vehicle body is where the different materials connect and contact, providing sites for corrosion to incubate and propagate [7, 8]. The most commonly observed types of corrosion that occurs are galvanic corrosion and crevice corrosion under such situations mentioned above [9].

Crevice corrosion is one type of local corrosion that occurs inside the minor crevice that formed on the surface of the alloy, usually of 0.025–0.1 mm in width, and has been widely investigated by researchers in the past. Crevice formers designed according to ASTM G48 were reported involving crevice corrosion [10]. In Jung et al.'s work, a Teflon shim was inserted in two steel plates which were connected by bolts and nuts [11]. The crevice formed in Jung's study was a skew crevice with a continuously changed width. Chengqiang Ren et al. designed a four-steel crevice in which four steel samples were embedded in the epoxy resin in a line [12]. This crevice former could be

Available online at <http://link.springer.com/journal/40195>

✉ Jin Li
corrosion@fudan.edu.cn

¹ Department of Materials Science, Fudan University, Shanghai 200433, China

Table 1 Composition of 316L stainless steel (wt.%)

	C	Si	Mn	P	S	Ni	Cr	Mo	Cu	N
316L	0.021	0.46	1.37	0.034	0.001	10.21	16.39	2.03	0.16	0.034

Table 2 Composition of epoxy carbon non-crimp fabric (wt.%)

Composite	Concentrate	Base material
Epoxy carbon non-crimp fabric (LE)	65	Epoxy resin

used to evaluate the influence of crevice corrosion as a function of crevice width [7, 13, 14]. Critical crevice corrosion potential, cyclic potentiodynamic polarization test and other techniques to evaluate the repassivation of crevice corrosion were reported to be used in characterizing alloys' crevice corrosion behaviors in typical crevice system in previous researches [10, 15–19]. Han et al. [10], and Yang et al. [20], studied crevice corrosion behaviors and mechanism of duplex stainless steels and the influences of pH, temperature and chloride concentration on crevice corrosion by electrochemical techniques and situ observation. In Karayan's work [18], a single-boss crevice former was presented and crevice corrosion behaviors were studied by repassivation corrosion potential technique.

However, there are not enough researches performed on crevice corruptions in the galvanic system and no relevant crevice former was mentioned for the applications yet. In this paper, we focused on the galvanic crevice former and evaluating techniques for crevice corrosion in the galvanic system. We designed the CFRP nuts to form the galvanic crevice and evaluated the galvanic system's impacts on crevice corrosion based on the devices by the repassivation potentials and revealed the mechanism for crevice corrosion in the galvanic system.

2 Experimental

In this paper, the galvanic couple composed of 316L stainless steel and the CFRP of epoxy carbon non-crimp fabric plates (EC) was studied. The chemical compositions of the two types of materials are list in Tables 1 and 2. The size of the samples was 20 mm × 30 mm × 2 mm with a 10-mm-diameter hole in the center. The samples were ground using 180-, 600- and 1000-grit abrasive papers, cleaned in deionized water and ethanol and dried at 60 °C for 24 h before the experiments [20, 21]. A conducting wire was spot welded to the 316L plate to hold the crevice assembly in the test solution and to provide an electrical contact during the test. The crevice former used in electrochemical research was made from polyformaldehyde (POM) and EC, as shown in Fig. 1. The crevice of the galvanic system was located at where EC and 316L plate contacted. The shape and dimension of the

Fig. 1 Schematic illustration of specimen assembly for crevice corrosion tests

crevice former followed the specification in ASTM G48 on the multiple crevice assembly. The crevice corrosion of the galvanic system was studied in 1 M NaCl solution at 30 °C. All measurements were carried out with a potentiostat of CHI660, which was connected to a typical three-electrode system. A platinum foil was used as the counter electrode (CE), and a saturated calomel electrode (SCE) was used as the reference electrode (RE). The CFRP-connected 316L plate worked as the working electrode (WE). The potentials mentioned in this paper were all referred to SCE. Before each test, the electrolyte was deaerated with pure nitrogen gas (N₂) for 30 min. The working electrode was cathodically polarized at $-0.9 V_{SCE}$ for 120 s. An open-circuit potential test was performed for 30 min in order to ensure a steady state surface of the specimen before each electrochemical test. After the electrochemical tests, the clearance gauge (KOSAKA ET3000) was used to measure the max and average corrosion depth of the morphology.

2.1 Potentiodynamic Polarization Test (PPT)

The potentiodynamic polarization test started at $-0.1 V$ versus open-circuit potential (OCP) at a scan rate of 0.167 mV/s. After 30 s, since the current density reached 100 $\mu A/cm^2$, the test was stopped. The potential when the current density reached 100 $\mu A/cm^2$ was defined as the critical crevice potential of the galvanic system, E_{cc} .

2.2 Cyclic Potentiodynamic Polarization Test (CPP)

The cyclic potentiodynamic polarization test started at $-0.1 V$ versus OCP at a scan rate of 0.167 mV/s. The

potential sweeping direction was reversed when the current density reached $40 \mu\text{A}/\text{cm}^2$, which indicated the initiation of crevice corrosion. The potential E_{rp1} corresponding to the intersection of the reversed current and the original passivation region, is defined as the repassivation potential.

2.3 Potentiodynamic-Galvanostatic-Potentiodynamic Reverse Scan (PGPD)

The potentiodynamic tests started at -0.1 V versus OCP at a scan rate of 0.167 mV/s until the current density reached $40 \mu\text{A}/\text{cm}^2$. Then, a galvanostatic test was applied at $40 \mu\text{A}/\text{cm}^2$ for 2 h. The third step of this technique was reversed potentiodynamic scan at a scan rate of 0.167 mV/s , from the potential where the last step ended. The repassivation potential E_{rp2} is the potential forward scan current and the reverse scan current intersect.

2.4 Potentiodynamic-Galvanostatic-Potentiostatic Reverse Scan (PGPS)

The first step of this technique, potentiodynamic test, started at -0.1 V versus OCP at a scan rate of 0.167 mV/s . Then, the galvanostatic test was applied at $40 \mu\text{A}/\text{cm}^2$ for 2 h. The third step, a series of potentiostatic tests, started from the last potential measured in the galvanostatic test and then stepped toward OCP at the increments of 10 mV , and each potentiostatic test was kept for 2 h. The potentiostatic test was terminated when the current density tended to remain constant as the function of time. The repassivation potential E_{rp3} is defined as the potential where the current density stopped increasing.

3 Results and Discussion

3.1 PPT

The obtained polarization curve is shown in Fig. 2, and SEM morphology of the specimen after the test is shown in Fig. 3. A typical corrosion morphology can be observed along the edge of the contacted area. This illustrated that crevice corrosion occurred in the galvanic system. According to the polarization results, E_{cc} of the galvanic system was measured to be $-0.025 \text{ V}_{\text{SCE}}$.

3.2 CPP

The cyclic potentiodynamic polarization curve of the galvanic system in 1 M NaCl solutions at 30°C is shown in

Fig. 2 Polarization curve of the galvanic system in 1 M NaCl solution at 30°C

Fig. 3 SEM Morphology of crevice corrosion for the galvanic system after potentiodynamic experiments in 1 M NaCl solution at 30°C

Fig. 4, and SEM morphologies of the samples after the tests are shown in Fig. 5. The morphologies illustrated that crevice corrosion occurred in this galvanic system. According to the polarization curve, E_{rp1} of this galvanic system is measured to be $-0.256 \text{ V}_{\text{SCE}}$. It was obviously observed from the polarization curves that the current did not decrease immediately as the potential sweeping direction started to reverse. The current kept increasing and then remained at a high level of about $10^{-4} \text{ A}/\text{cm}^2$ for a short while, indicating that the crevice corrosion kept growing when the sweeping potential started to reverse. The current started to decrease when the reverse scan reached the potential of $-0.1 \text{ V}_{\text{SCE}}$. Therefore, in this galvanic system of SS 316L and CFRPs, crevice corrosion could not keep propagating and the stainless steel surface began to repassivate if the polarization potential decreased below $-0.1 \text{ V}_{\text{SCE}}$.

Fig. 4 Cyclic potentiodynamic result of the galvanic system in 1 M NaCl solution at 30 °C

By comparing the morphologies of crevice corrosion in Figs. 3 and 5, we can observe an additional metastable pitting that is located besides the crevice edge and inside the crevice area after the reversed potential sweeping, as shown by Fig. 5b. In the previous research, it has been reported that, metastable pitting corrosion happens during the initiation period of the crevice corrosion, which is the original source of the corrosion propagating [22]. Corrosion in the crevice kept inducing, and crevice solution was acidized as the potential increasing. According to the previous study [15], the critical condition for crevice corrosion is the chloride concentration of 2.5 M and the pH value of 2.1. After the potential decreased to $-0.1 \text{ V}_{\text{SCE}}$ during the reversed scan, the environment beneath the crevice could not meet the requirements of critical condition, crevice corrosion stopped propagating and the stainless steel surface started to repassivate. During the repassivation period, the metastable pitting

kept growing that explained the results observed in the SEM morphologies.

3.3 PGPD

The PGPD curve for the galvanic system in 1 M NaCl solution at 30 °C is given in Fig. 6, and SEM morphologies for the samples after the tests are shown in Fig. 7. The morphology confirmed the occurrence of crevice corrosion in the galvanic system under such technique, and E_{rp2} was measured to be $-0.122 \text{ V}_{\text{SCE}}$. During the galvanostatic tests, the static current of $40 \mu\text{A}/\text{cm}^2$ was applied to the galvanic system of SS 316L and CFRPs, which limited crevice corrosion's initiation rate but did not stop it. The measured potential decreased during the galvanostatic tests, and once the applied current stopped and the potential sweeping direction reversed, the current decreased rapidly and reached the repassivation level. It could be revealed

Fig. 6 Potentiodynamic-galvanostatic-potentiodynamic curve of the galvanic system in 1 M NaCl solution at 30 °C

Fig. 5 SEM Morphologies of crevice corrosion in the galvanic system after cyclic potentiodynamic experiments in 1 M NaCl solution at 30 °C: **a** the whole crevice area, **b** metastable pitting besides the crevice edge

Fig. 7 SEM morphologies of crevice corrosion for galvanic system after potentiodynamic-galvanostatic-potentiodynamic experiments in 1 M NaCl solution at 30 °C: **a** the whole crevice area, **b** metastable pitting inside the crevice

Fig. 8 Measured potential, current as the function of time in potentiodynamic-galvanostatic-potentiostatic test in 1 M NaCl solution at 30 °C

from the morphologies of specimens after CPP and PGPD tests, respectively, that the larger and deeper corroded area existed on the surface of specimens that underwent PGPD tests which resulted from 2-h galvanostatic test. A lot of metastable pitting could be observed near the crevice mouth as shown in Fig. 7b.

3.4 PGPS

In the PGPS technique, the corrosion current induced by the applied potential is close to the stable state because the long period for the applied potentials of 2 h. In the actual conditions, the corrosion currents are also defined in the steady state. The $E/I-t$ curves obtained from the PGPS tests are shown in Fig. 8, and SEM morphologies for the specimens after those tests are shown in Fig. 9. The morphologies proved crevice corrosion did occur in this galvanic system. E_{rp3} of the galvanic system of 316L and CFRP was measured to be $-0.1 V_{SCE}$ according to the curves. The measured

currents were dynamic currents in the previous two cyclic polarization tests and were static currents in PGPS tests; the measured repassivation potential here was closer to actual conditions because of the relatively long quiescent initiation period for crevice corrosion. The morphologies for specimens after PGPS tests were similar as those after PGPD tests, while the specimens after PGPS tests had larger corrosion area than those after PGPD tests. At the central part of the corroded zone, grain boundary could be easily observed, which illustrated the acidized crevice environment. Obvious current fluctuations could be observed from the $E/I-t$ curves, indicating the existence of metastable pitting before reaching the repassivation potential, as revealed in Fig. 9. Current kept increasing in each potentiostatic period until the potential decreased to the repassivation potential. It demonstrated that during each potentiostatic test period, crevice corrosion continued to grow at a much slower rate than that during potentiodynamic test.

The repassivation potentials acquired from three electrochemical techniques mentioned above and the max and average depth of the corrosion sites are listed in Table 3. The maximum difference among the three potentials was $0.156 V_{SCE}$, which resulted from the 2-h galvanostatic test period in both PGPD and PGPS tests and a longtime potentiostatic period in PGPS test for crevice corrosion to grow. Through PGPD and PGPS tests we could gain the morphology for the whole stages of crevice corrosion. Through PGPS tests we could get the repassivation potential high close to actual conditions and simulate the whole process of the initiation, propagating and repassivation stages of crevice corrosion. As a result, we could use the corrosion morphologies obtained from PGPS tests to investigate the crevice corrosion behaviors in the galvanic system of SS 316L and CFRPs.

The morphology in Fig. 9a could be divided into four zones. Zone-I presents the initiation stage of crevice corrosion (Fig. 9b). Zone-II is the propagating stage (Fig. 9c).

Fig. 9 SEM morphologies of crevice corrosion for galvanic system after potentiodynamic-galvanostatic-potentiostatic experiments in 1 M NaCl solution at 30 °C: **a** the whole corrosion, **b** Zone-I, **c** Zone-II, **d** Zone-III, **e** Zone-IV

Table 3 Repassivation potentials and corrosion depth obtained from the three electrochemical techniques

	Repassivation potential (V)	Max corrosion depth (μm)	Average corrosion depth (μm)
CPP	-0.256 ± 0.012	2.32	1.67 ± 0.60
PGPD	-0.122 ± 0.021	84.15	64.77 ± 9.83
PGPS	-0.100 ± 0.010	97.79	69.71 ± 12.28

Zone-III is the uniform corrosion stage (Fig. 9d), and Zone-IV is the crevice mouth (Fig. 9e). In the crevice mouth zone, it is possible for ions to exchange between crevice mouth zone and bulk solution outside the crevice and it is therefore difficult for pH value and chloride concentration to reach the critical conditions for crevice corrosion to initiate. Only metastable pitting is observed in Zone-IV. Zone-III locates besides the crevice mouth and it is hard for ions to transfer from this zone to the solution outside the crevice, which results in the accumulation of Cl^- and H^+ until pH and Cl^- concentration meet the critical condition of crevice corrosion where corrosion will happen.

It should be noted that one of the most important conditions for crevice corrosion is the crevice size. Crevice corrosion will stop once the crevice size exceeds the critical size for crevice corrosion as the corrosion process goes on. That explains the hardly observed metastable pitting in Zone-III, and hence no crevice corrosion but general corrosion existed there. In Zone-II, there are lots of metastable pits on the alloy surface, which indicates the development of

crevice corrosion depends on the initiation and expanding of the metastable pitting. Zone-I is the deepest area inside the crevice. Species of Cl^- and H^+ diffuse into Zone-I as the corrosion elsewhere beneath the crevice goes on, leading to the initiation of quantities of metastable pitting in the zone. Crevice corrosion is expected to initiate and grow when the critical conditions are reached here.

The mechanism of crevice corrosion in the galvanic system of SS 316L and CFRPs is summarized as four steps described in Fig. 10 according to the discussion above. At Step A, as a crevice sample is immersed into solution, the hydrolysis reactions attributed to the stainless steel happen on the alloy surface that leads to the minor amount of accumulation of H^+ and Cl^- in the crevice mouth zone. As it is smooth for ions exchange in the crevice mouth zone, the solution environment keeps stable and hence no crevice corrosion happens as indicated by the morphology of Zone-IV. Only small amounts of repassivated metastable pitting are observed in this area. At step B, the dissolved oxygen in the crevice is gradually consumed by the cathodic reactions and cannot be replenished because of the difficulty for ion exchange through the crevice mouth. The cathodic reactions are therefore shifted to the outside surface, and only anodic reaction by which the alloy dissolves that can happen inside the crevice. Crevice corrosion begins to initiate as the critical condition for crevice corrosion has been met that attributed to the acidification of the crevice solution and the diffusion of the chloride into the crevice. Metastable pitting corrosion occurs in this stage, and stable crevice corrosion will generate as the metastable pitting has adequately grown

Fig. 10 Schematic diagram of crevice corrosion generating process in 316L-CFRP galvanic system

and expanded. The morphology of this stage is described as Zone-I. At step C, crevice corrosion grows at a considerable rate. The corrosion growing direction is vertically downward the crevice mouth and the same as chloride transferring direction driven by the electric field force into the crevice. Metastable pitting can still generate on the already corroded surface, which is shown in Fig. 9c. The morphology of this stage is described as Zone-II which presents the larger depth compared with Zone-I. At step D, the crevice corrosion sufficiently propagates and the size of the crevice exceeds the critical crevice size, leading to the ending of the crevice corrosion. General corrosion occurs instead in this zone, as demonstrated by Zone-III.

3.5 Influence of Galvanic System on Crevice Corrosion

SS 316L surface can be polarized without applied potential in the corrosive environment because of the galvanic system. The processes of initiation, propagation and repassivation of the crevice corrosion are all influenced by the galvanic

system. The polarization curves for 316L stainless steel with the normal crevice maker and the galvanic couple, respectively, are shown in Fig. 11. The normal crevice system is designed by ASTM G48.

At the initiation period of crevice corrosion, the self-corrosion potential of the galvanic system is driven away from the normal crevice system's self-corrosion potential, and hence the balance between anodic and cathodic reactions breaks up. Anodic reaction rate exceeds that of cathodic reactions, resulting in the increase in concentration of Fe^+ cations and the decrease in concentration of OH^- anions. Solution in the crevice acidizes faster than the stainless steel in the normal crevice system. To maintain electric neutrality, Cl^- anions diffused into the crevice by the electric field force, which shortens the initiation period. As the curves shown in Fig. 11, self-corrosion current density and passivation current density in galvanic system are higher than that in normal crevice system, while the passivation zone of polarization curves of galvanic system is narrower than that of normal crevice system. During the growing period, corrosion current density slopes more than that of the normal

Fig. 11 Polarization of SS 316L with crevice former in galvanic, non-galvanic system

crevice system, which indicates the higher rate of crevice corrosion growing.

4 Conclusions

In this study, we designed a crevice former made of CFRP to generate a galvanic crevice and evaluated the crevice corrosion behaviors in the galvanic system by four types of electrochemical techniques. The maximum difference between the three repassivation potentials was 0.156 V, which resulted from the 2-h galvanostatic test period in both PGPD and PGPS tests, and through PGPS tests, we could get the repassivation potential that is the closest to actual conditions and simulate the whole process of the initiation, propagation and repassivation stages of crevice corrosion.

The crevice corrosion of galvanic systems grew along the crevice from crevice mouth to the inside crevice and could be divided into four stages as mentioned. Under the impact of galvanic systems, stainless steels were driven away from its self-corrosion potential which speeded up electrode reaction rates and shortened the passivation zone at the initiation stage of crevice corrosion. In the galvanic system, corrosion rate was therefore higher than that in normal crevice system.

Acknowledgements This work was supported by National Key Research and Development Program of China (Grants No. 2018YFB0704400) and National Natural Science Fund of China (Grants Nos. 51671059, 51871061, 51801028). The authors also greatly acknowledge the help provided by Mr. Gang Hu in SEM characterization and would like to thank the helpful collaboration of General Motors Corporation.

References

- [1] R. Arrabal, A. Pardo, M.C. Merino, M. Mohedano, P. Casajus, K. Paucar, G. Garces, *Corros. Sci.* **55**, 301 (2012)
- [2] L. Arronche, K. Gordon, D. Ryu, V. La Saponara, L. Cheng, *J. Mater. Sci.* **48**, 1315 (2013)
- [3] S.C. Ferreira, L.A. Rocha, E. Ariza, P.D. Sequeira, Y. Watanabe, J.C.S. Fernandes, *Corros. Sci.* **53**, 2058 (2011)
- [4] F. Bellucci, A. Di Martino, C. Liberti, *J. Appl. Electrochem.* **16**, 15 (1986)
- [5] M. Mandel, L. Krüger, *Materialwiss Werkst* **43**, 302 (2012)
- [6] G.T. Burstein, S.P. Vines, *J. Electrochem. Soc. B* **148**, 504 (2001)
- [7] M. Bryant, R. Farrar, R. Freeman, K. Brummitt, J. Nolan, A. Neville, *J. Mech. Behav. Biomed.* **40**, 275 (2014)
- [8] B.P. Cai, Y.H. Liu, C.K. Ren, Z.K. Liu, X.J. Tian, A.B.B. Abulimiti, *Corros. Eng., Sci. Technol.* **47**, 289 (2012)
- [9] G.D. Franco, L. Fratini, A. Pasta, *Mater. Des.* **35**, 342 (2012)
- [10] D. Han, Y.M. Jiang, C. Shi, B. Deng, J. Li, *J. Mater. Sci.* **47**, 1018 (2012)
- [11] J.Y. Jung, S.Y. Park, H.J. Won, S.B. Kim, W.K. Choi, J.K. Moon, S.J. Park, *J. Radioanal. Nucl. Ch.* **306**, 377 (2015)
- [12] C. Ren, J. Chen, L. Pu, L. Liu, Y. Pan, J. Hu, T. Shi, *Int. J. Electrochem. Soc.* **10**, 8210 (2015)
- [13] A.K. Mishra, G.S. Frankel, *Corrosion-Houston Tx* **64**, 397 (2008)
- [14] S.T. Arab, M.I. Abdulsalam, H.M. Alghamdi, *Arab. J. Sci. Eng.* **39**, 5405 (2014)
- [15] J.W. Oldfield, W.H. Sutton, *Brit. Corros. J.* **13**, 13 (1977)
- [16] T. Li, L. Liu, B. Zhang, Y. Li, F. Wang, *J. Electrochem. Soc.* **162**, C354 (2015)
- [17] S. Marcelin, N. Pébère, S. Régnier, *J. Electroanal. Chem.* **737**, 198 (2015)
- [18] A.I. Karayan, J.E. Guerrero, H. Castaneda, *J. Alloys Compd.* **619**, 544 (2015)
- [19] J. Wang, S. Qian, Y. Liu, Y. Sun, Y. Jiang, J. Li, *Acta Metall. Sin. (Engl. Lett.)* **31**, 815 (2018)
- [20] Y.Z. Yang, Y.M. Jiang, J. Li, *Corros. Sci.* **76**, 163 (2013)
- [21] X. Chen, F. Gao, Y. Wang, C. He, *Mater. Des.* **89**, 196 (2016)
- [22] J.W. Oldfield, W.H. Sutton, *Brit. Corros. J.* **13**, 104 (1978)