

Model Cut-edge Formed on Zinc Coated Steels by Laser Machining and Its Corrosion Behavior

Masatoshi Sakairi[†], Akihiro Kageyama, and Tatsuya Kikuchi

Division of Materials Science and Engineering, Graduate School of Engineering, Hokkaido University
Kita-13, Nishi-8, Kita-ku, Sapporo, 060-8628, Japan

(Received July 28, 2009; Revised February 19, 2010; Accepted February 20, 2010)

Laser machining technique, which is used focusing pulse YAG laser beam irradiation was applied to form area ratio controlled model cut-edge on pre painted Zn coated steels. A corrosion behavior of formed model cut-edge was investigated by rest potential measurement in 1 mol m⁻³ NaCl with and without 0.5 kmol m⁻³ H₃BO₃/0.05 kmol m⁻³ Na₂B₄O₇. The rest potential showed almost constant value with fluctuations. The amplitude of fluctuations increased with exposed area of steel surface. White corrosion products of zinc oxide and simonkollite was formed after the experiments at the formed model cut-edge.

Keywords : cut edge, corrosion, Zn coating, chromate, laser

1. Introduction

Zinc or zinc alloy coated steels are widely used, because of their high corrosion resistance in many corrosive environments. Therefore many book and papers related to corrosion of the coated steels were published.¹⁾⁻⁹⁾ One of the weak regions of the coated steels for corrosion is the cut-edge face, which is formed while machining to fabricate on it. In general situation, no further coating process will carry out at the cut edge face. Until now, Cr⁶⁺ ions related surface treatment and presence of Cr⁶⁺ related chemicals in paint reduce the corrosion rate of metals at cut-edge in many corrosive environments. Cr⁶⁺ ion is highly hazardous substance. The hazardous substances are prohibited from using for industrial products by some standard, such as RoHS and ELV. The recent situation becomes more severe for cut-edge corrosion of coated steels. Therefore, many researchers in Japan have been studied the cut-edge corrosion using model cut-edge, which is formed by machining.¹⁰⁾

This type of model cut-edge suffers from burr and controlling exposed ratio, $S_r = \text{coated layer area}/\text{steel substrate area}$. To avoid burr and control S_r , pulsed YAG Laser fabrication technique was applied to form model cut-edge on pre painted Zn coated steels. The purpose of this study is to investigate effect of S_r on corrosion behavior of model cut-edge formed pre painted Zn coated steels by electro-

chemical technique.

2. Experimental

2.1 Specimen

Two different pre painted Zn coated steels, chromate free painting (Zn-CF) and chromate containing painting (Zn-CR), were used as specimen. The size of the sheets was 15 x 20 mm. Before the experiments, Specimens were cleaned in doubly distilled water and an ethanol ultrasonic bath. Fig. 1 shows schematic drawing of top view and cross section of specimen.

2.2 Formation of model cut-edge

To form model cut edge, specimens were irradiated by a focused Nd-YAG laser beam (Sepctra Physics GCR-130, wave duration 8 ns, frequency 10 s⁻¹, wave length 532 nm) in 0.5 kmol m⁻³ H₃BO₃ / 0.05 kmol m⁻³ Na₂B₄O₇

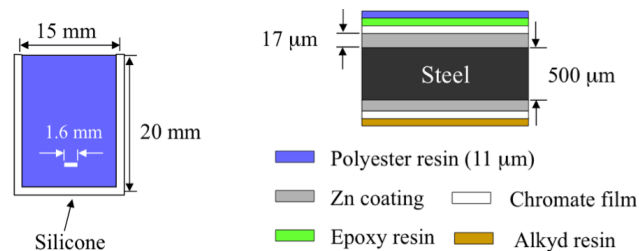


Fig. 1. Schematic drawing of top and cross sectional view of specimen.

[†] Corresponding author: msakairi@eng.hokudai.ac.jp

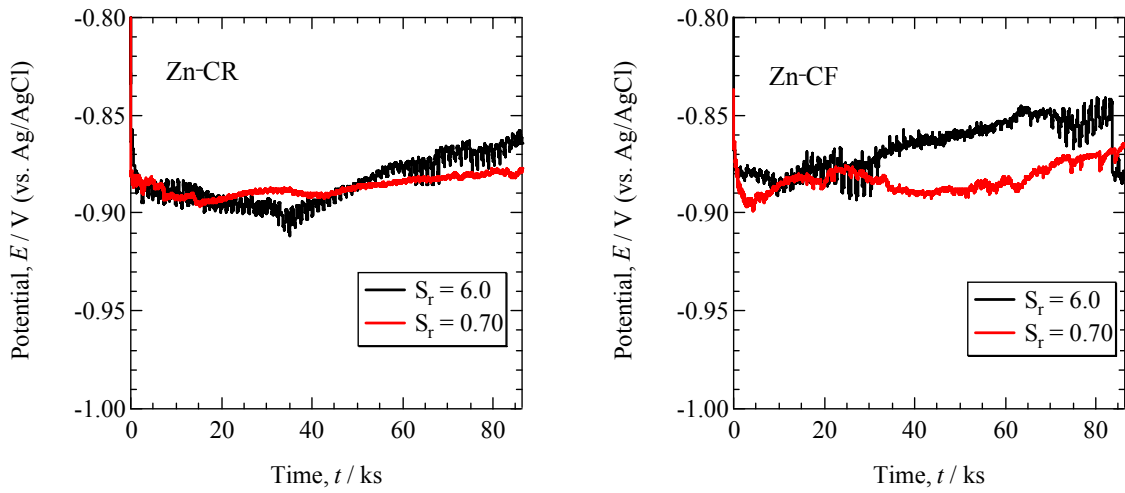


Fig. 2. Changes in rest potential of model cut edge formed Zn-CR and Zn-CF in 0.01 kmol m^{-3} NaCl.

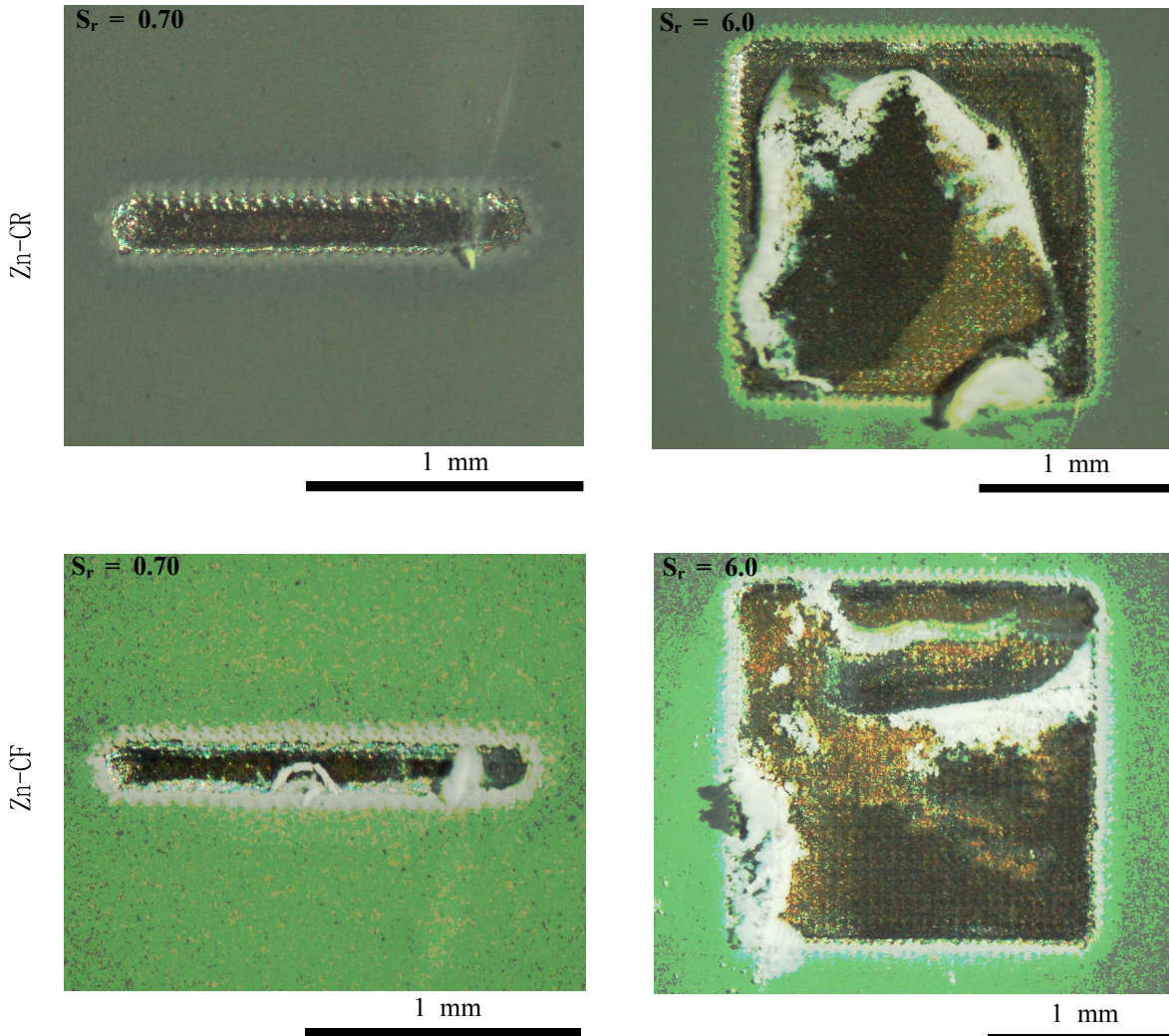


Fig. 3. Optical images of Zn-Cr and Zn-CF after the rest potential measurement in 0.01 kmol m^{-3} NaCl.

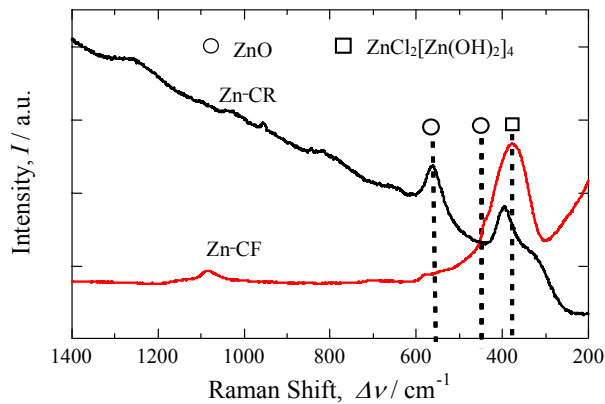


Fig. 4. Raman spectrum of white corrosion products in fig. 3.

solutions, while laser beam irradiation, specimens were moved by X-Y stage to control $S_r = 0.7$ to 6.0. The laser beam power was adjusted to 20 mW in front of the lens.

2.3 Corrosion tests

After formation of model cut edge, specimens were dipped in 0.1 mol m^{-3} NaCl and measured rest potential. In some experiments, only 0.1 mol m^{-3} NaCl with 0.5 kmol m^{-3} $\text{H}_3\text{BO}_4/0.05 \text{ kmol m}^{-3}$ $\text{Na}_2\text{B}_4\text{O}_7$ solution was used to investigate effect of buffer reaction on corrosion behavior of the model cut edge.

2.4 Surface analysis

After the experiments, specimen surfaces were exam-

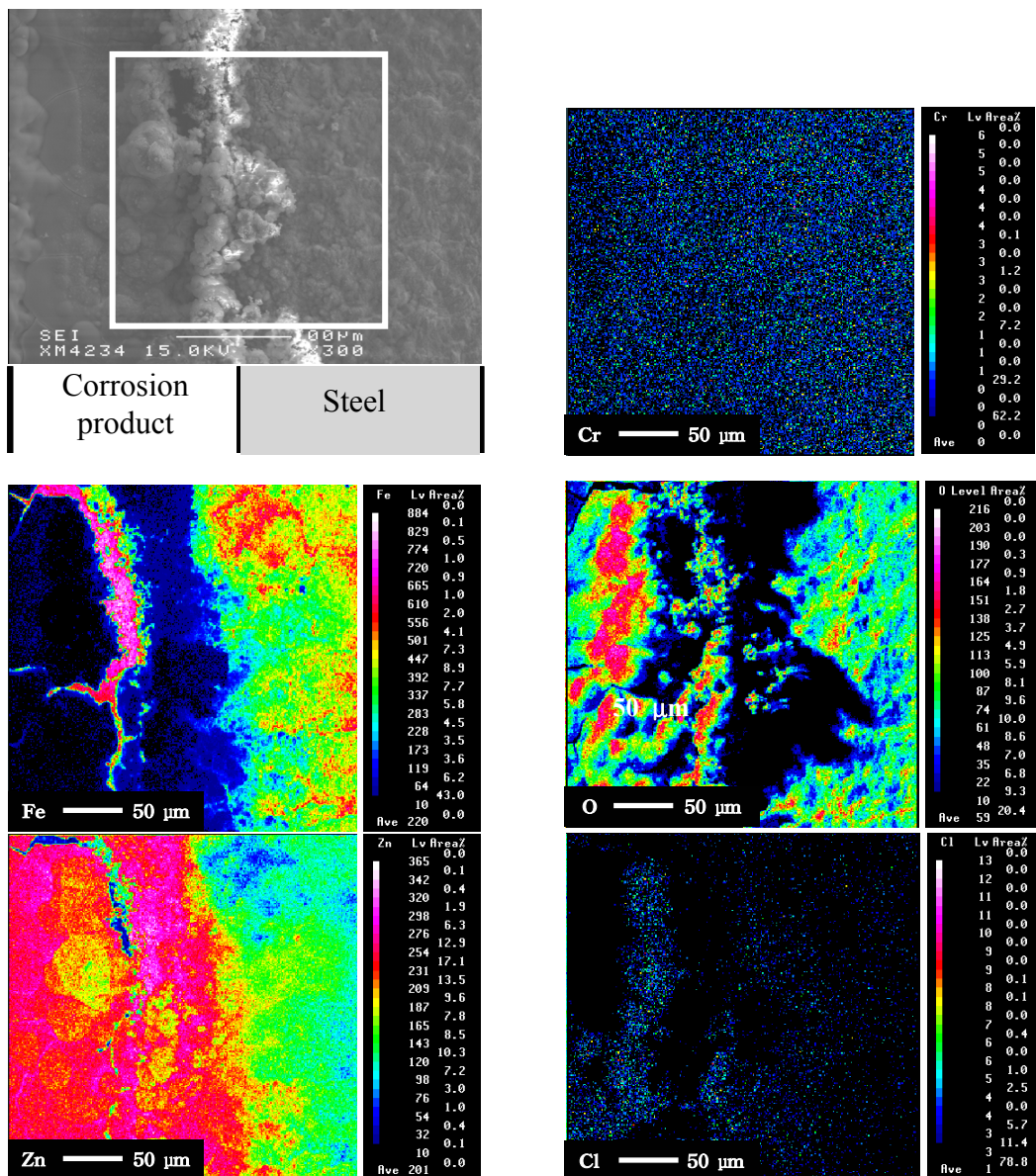


Fig. 5. SEM and EPMA element mapping of Zn-CR after rest potential measurement in 0.01 kmol m^{-3} NaCl.

ined by optical microscope and scanning electron microscope. To analysis composition and structure of formed corrosion products, Electron probe X-ray micro-analyzer and Laser Raman spectroscopy were used.

3. Result and discussion

3.1 Corrosion test in NaCl solutions

Fig. 2 shows changes in rest potential of model cut edge formed on Zn-CR and Zn-CF in 0.01 kmol m^{-3} NaCl. After specimens dipped in the solution, rest potential decrease suddenly to about -0.9 V then increase slowly with immersion time. The rest potential does not affected by S_r and existence of chromate, however, the fluctuations of rest potential becomes larger with increasing S_r in both Zn-CR and Zn-CF.

Fig. 3 shows optical surface images of after the corrosion tests of Zn-CR and Zn-CF specimens. White corrosion products are shown at formed model cut edge. Because cathodic reaction was accelerated by exposed area of steel substrate, the volume of corrosion products is increased with increasing S_r in both CR and CF specimen. From the optical images, volume of corrosion products on Zn-CR is smaller than that on Zn-CF. This result indicated that chromate reduces dissolution of zinc from the coating.

The structure was investigated by EPMA and Raman spectroscopy. Fig. 4 shows Raman spectrum of white rust shown in Fig. 3. From EPMA element mapping analysis (Fig. 5), Zn, Cl and O are observed at white rust. There are peaks around 370 , 440 and 570 cm^{-1} in Raman spectrum. Both Raman spectrum and EPMA element analysis, white rust may be zinc oxide, ZnO and simonkolleite, $\text{ZnCl}_2[\text{Zn}(\text{OH})_2]_4\text{H}_2\text{O}$.¹¹⁾

3.2 Corrosion test in NaCl with $0.5 \text{ kmol m}^{-3} \text{ H}_3\text{BO}_4/0.05 \text{ kmol m}^{-3} \text{ Na}_2\text{B}_4\text{O}_7$

Fig. 6 shows changes in rest potential of model cut edge formed Zn-CR in 0.1 mol m^{-3} NaCl with $0.5 \text{ kmol m}^{-3} \text{ H}_3\text{BO}_4/0.05 \text{ kmol m}^{-3} \text{ Na}_2\text{B}_4\text{O}_7$. The tendency of rest potential is almost same as in Fig. 2, however, the rest potential shift to positive direction with increasing S_r . The amplitude of current fluctuations also increases with increasing S_r .

Fig. 7 shows optical surface images of after the corrosion tests of Zn-CR specimens after the corrosion test. White corrosion products are shown at formed model cut edge of $S_r = 6.0$. On the contrast, no corrosion products were seen on $S_r = 0.70$ and 1.4 specimens. This result suggests that dissolution rate or precipitation mechanism of zinc is affected by solution pH.

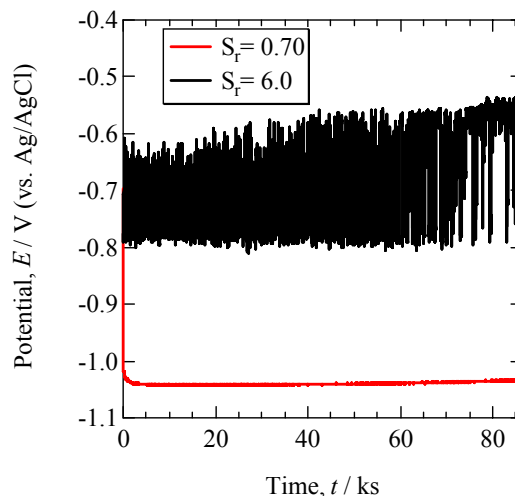


Fig. 6. Changes in rest potential of model cut edge in 0.1 mol m^{-3} NaCl with $0.5 \text{ kmol m}^{-3} \text{ H}_3\text{BO}_4/0.05 \text{ kmol m}^{-3} \text{ Na}_2\text{B}_4\text{O}_7$.

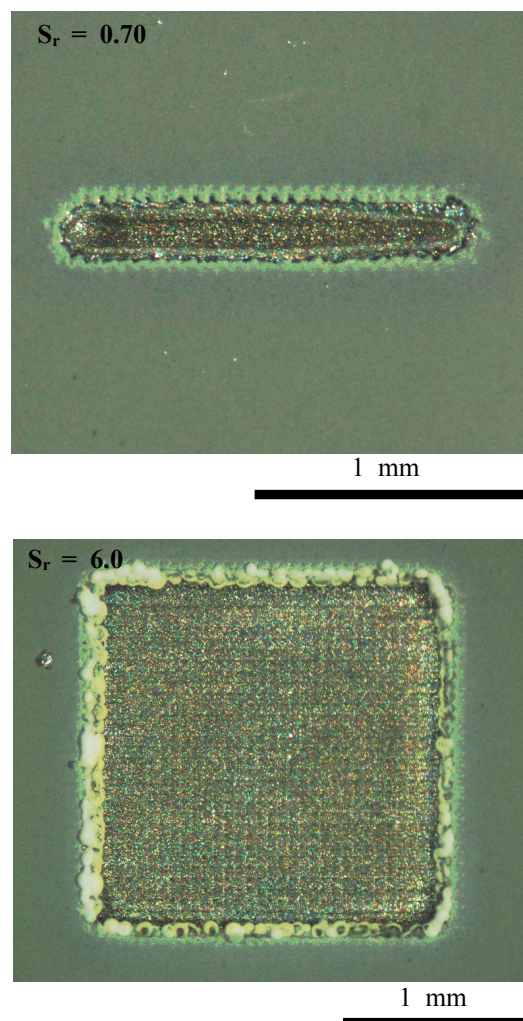


Fig. 7. Optical micrographs of Zn-CR after rest potential measurement in 0.01 kmol m^{-3} NaCl with $0.5 \text{ kmol m}^{-3} \text{ H}_3\text{BO}_3 / 0.05 \text{ kmol m}^{-3} \text{ Na}_2\text{B}_4\text{O}_7$.

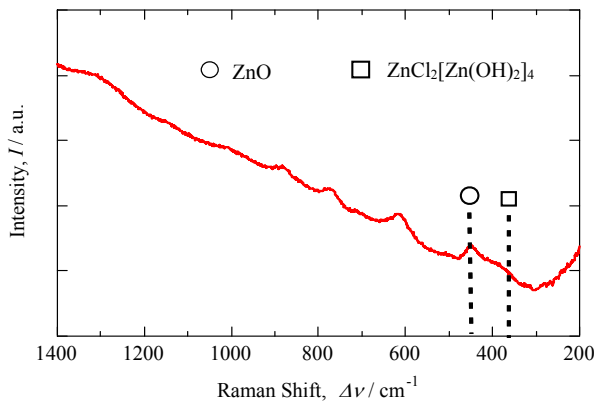


Fig. 8. Raman spectrum of white corrosion products in fig. 7.

Fig. 8 shows Raman spectrum of white rust in Fig. 5. There are peaks around 370 and 440 cm^{-1} . From EPMA element mapping analysis, Zn, Cl and O were observed at white rust. Both Raman spectrum and EPMA element analysis, the white corrosion products may be zinc oxide, ZnO and simonkolleite, $\text{ZnCl}_2[\text{Zn}(\text{OH})_2]_4\text{H}_2\text{O}^{11)}$

4. Conclusions

The immersion corrosion tests of model cut edge formed specimens were carried out. Following conclusions can be drawn.

- 1) In all specimens expect to specimen of $S_r = 0.70$ exposed in NaCl with $0.5 \text{ kmol m}^{-3} \text{ H}_3\text{BO}_3/0.05 \text{ kmol m}^{-3} \text{ Na}_2\text{B}_4\text{O}_7$. The white corrosion products are observed and the volume of corrosion products increases with S_r .
- 2) The rest potential fluctuations are observed in high S_r specimens, and these are increased with increasing S_r in both solutions.
- 3) From Raman spectroscopy and EPMA element mapping analysis, it is proved that compositions of white cor-

rosion products formed on the model cut edge formed specimens are zinc oxide and simonkolleite.

Acknowledgments

This study was carried out under the research project of "Research Report for CutEdge Corrosion Mechanism and Life Predictions of Pre Painted Steel Sheets for Residential Use", The Iron and Steel Institute of Japan.

References

1. The Iron and Steel Institute of Japan, Research Report for Fundamentals of Corrosion Protection and Evaluation Methods on Zinc Alloy Coated Steels, Tokyo (2005).
2. X. G. Zhang, Corrosion and Electro-chemistry of Zinc, Plenum Press, New York (1996).
3. H. E. Townsend and J. G. Zoccola, *Material Performance*, **18**, 13 (1979).
4. H. Shindo, K. Nishimura, and K. Kato, *Proc. of Galvatech*, **98**, 433 (1998).
5. S. Fujita, M. Yoshida, T. Odajima, T. Kanemaru, and Y. Shindo, *Tetsu to Hagane*, **81**, 54 (1995).
6. G. A. El-Mahdy, A. Nishikata, and T. Tsuru, *Corros. Sci.*, **42**, 183 (2000).
7. R. Lindstrom, J. E. Svensson, and L. G. Jahnsson, *J. Electrochem. Soc.*, **147**, 1751 (2000).
8. M. Sakairi, Y. Uchida, and H. Takahashi, *ISIJ Int.*, **46**, 1218 (2006).
9. M. Sakairi, Y. Uchida, and H. Takahashi, *Corros. Sci.*, **49**, 2362 (2007).
10. The Iron and Steel Institute of Japan, Research Report for CutEdge Corrosion Mechanism and Life Predictions of Pre Painted Steel Sheets for Residential Use, Tokyo (2009).
11. T. Ohtsuka and Y. Abe, *Proc. of GALVATEC'07* (2007) 648.