# Pitting Corrosion of Ni$_3$(Si,Ti)+2Cr Intermetallic Compound at Various Chloride Concentrations

Gadang Priyotomo[#1], Pius Sebleku[#], Yasuyuki Kaneno[*2]

*#Research Center for Metallurgy, Indonesian Institute of Sciences*
*Kawasan PUSPIPTEK Gd.474, Setu, Tangerang Selatan, Banten, Indonesia*
[1]gadangp@gmail.com
*\*Department of Materials Science, Graduate School of Engineering, Osaka Prefecture University*
*1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan*
[2]kaneno@mtr.osakafu-u.ac.jp

Abstract - The pitting corrosion of Ni$_3$(Si,Ti) with 2 at% Cr containing two regions of a Ni$_3$(Si,Ti) single-phase of L1$_2$ structure and a mixture phase of of (L1$_2$ +Ni$_{ss}$) was investigated as function of chloride concentrations by using a polarization method, scanning electron microscope and energy dispersive X-Ray spectroscopy in neutral sodium chloride solutions at 293 K. The pitting corrosion of Ni$_3$(Si,Ti) with and without the addition of aluminium and type C276 alloy were also studied under the same experimental condition for the comparison. The pitting potential obtained for the Ni$_3$(Si,Ti) with 2 at% Cr decreased with increasing chloride concentration. The specific pitting potentials and the pitting potentials were decreased in the order of C276 alloy > Ni$_3$(Si,Ti) > Ni$_3$(Si,Ti) + 2Cr > Ni$_3$(Si,Ti) + 4Al, which means that the pitting corrosion resistance of Ni$_3$(Si,Ti) with 2 at% Cr was higher than Ni$_3$(Si,Ti) with 4 at% Al, but lower than that of Ni$_3$(Si,Ti). A critical chloride concentration of Ni$_3$(Si,Ti) with 2 at% Cr was found to be higher than that of Ni$_3$(Si,Ti) with at% Al. In addition, the presence of high concentration for oxygen indicates the occurrence of pit formation.

Keywords : Intermetallic Compound; Pitting Corrosion; Sodium Chloride; Polarization, Scanning Electron Microscope, Energy Dispersive X-Ray Spectroscopy

## I. INTRODUCTION

The nickel base intermetallic compounds such as Ni$_3$(Si,Ti) with and without addition of chromium (Cr), showing a high melting temperature, have advantages of lightweight and high-temperature oxidation resistance compared with conventional alloys such as steel and nickel-based alloys (Takasugi et al.,1990 ; Kaneno et al., 2011). Therefore, those intermetallic compounds could be applied as high-temperature materials in the future (Takasugi et al., 2002). On the other hand, an improvement in the oxidation resistance of the Ni$_3$(Si,Ti) intermetallic compound was attempted with macro-alloying by adding Cr, which enhanced that resistance at high temperatures (Kaneno et al.,2011).

Furthermore, Ni$_3$(Si,Ti) with 2 at.% Cr were composed of two regions of the L1$_2$ single-phase and a two phase mixture of L1$_2$ and Ni$_{ss}$, where Ni$_{ss}$ was a fcc Ni solid solution as well as the Ni$_3$(Si,Ti) with Mo and Al (Kaneno

et al., 2011). In addition, it was also found that the addition Cr was slightly effective in improving high-temperature ductility property (Fujimoto et al.,2011). On the Ni$_3$(Si,Ti) with 2 at.% Cr, before conducting polarization test, Gadang and co-workers also found that the main element of Ni was present uniformly (Priyotomo et al.,2012). On this compound, Cr was enriched in the two phase region of L1$_2$ and Ni$_{ss}$, while Ti and Si are enriched in the L1$_2$ single-phase region ( Priyotomo et al.,2012)4. However, the Ni$_3$(Si,Ti) intermetallic compounds are prone to environmental embrittlement (hydrogen embrittlement) at room temperature in moist environment (Takasugi et al.,1993a,b), where that embrittlement takes place with permeation of atomic hydrogen through electrochemical reaction into the bulk of the compounds.

Up to the present, the intermetallic compound such as Ni$_3$(Si,Ti) with the addition of Cr have not systematically

been investigated for the pitting corrosion behavior in neutral chloride concentration. On the other hand, the pitting corrosion behavior of Ni₃(Si,Ti) with and without addition of Mo and Al already were investigated in neutral chloride solution (Wagle et al., 2011a,b ; Priyotomo., 2013).

Therefore, the aim of this work is to explain the pitting corrosion behavior of Ni₃(Si,Ti) with addition of 2 at % Cr in various chloride concentrations at 293 K and to compare with that of Ni₃(Si,Ti) intermetallic compound without and with Al, and C-276 alloy as the references (Priyotomo, 2013 ; Priyotomo et al,2014).

## II. EXPERIMENTAL

### A. The specimens

Ni–11 at.% Si– 7.5 at.% Ti–2 at.% Cr compound with the addition of 50 wt. ppm (part per million) of boron (B) was made by using an arc melting method under an argon gas atmosphere in a very high vacuum electric furnace. It was homogenized at 1323K for 48 hours under argon atmosphere and then cooled in the high vacuum furnace with cooling rate of 283 K/ min. C276 alloy, Ni₃(Si,Ti) compound (Priyotomo et al.,2013) and Ni₃(Si,Ti)+4Al compound (Priyotomo et al.,2014) also were as the references for the experiments. The chemical and nominal compositions of materials are shown in Table 1.

Table 1: Composition and nominal of the materials investigated

| Elements | Ni₃(Si,Ti) +2Cr | Ni₃(Si,Ti) +4Al* | Ni₃(Si,Ti)** | C276** |
|---|---|---|---|---|
| | **At%** | | | |
| C | - | - | - | 0.02 |
| Si | 11.0 | 11.0 | 11.0 | 0.08 |
| Mn | - | - | - | 1.00 |
| P | - | - | - | 0.03 |
| S | - | - | - | 0.03 |
| Ni | 79.5 | 79.5 | 79.5 | 50.99 |
| Cr | 2.0 | - | - | 16.5 |
| Mo | - | - | - | 17 |
| V | - | - | - | 0.35 |
| Fe | - | - | - | 7 |
| Ti | 7.5 | 5.5 | 9.5 | - |
| W | - | - | - | 4.5 |
| Co | - | - | - | 2.5 |
| Al | - | 4.0 | - | - |
| | **ppm** | | | |
| B | 50 | 50 | 50 | - |

*(Priyotomo et al.,2014) and **(Priyotomo et al.,2013)

For the microstructure observation, a galvanostatic etching of the mechanically polished specimens was conducted in a solution consisting of 15 ml of 17.8 kmol/m³ $H_2SO_4$ and 85 ml of methanol at a current density of 0.446 A/cm² for 30 seconds (s) at a temperature of 243 K.

### B. Polarization test

The specimens were polished with silica carbide paper up to 1200 grit and then were rinsed with distilled water and cleaned in an acetone ultrasonic bath. The test solutions were neutral sodium chloride solutions with various chloride concentrations (0.00001 to 1 kmol/m³), which were made with the distilled water and high grade chemical reagent. The test temperatures used was 293 K. The polarization experiments were carried out in a round bottom cell of 1000 ml capacity using a potentiostat apparatus (Reference 600,Gamry Instrument), interfaced to a personal computer. The potential values were measured by using a reference electrode of a saturated calomel electrode (SCE). All potentials referred in this work are with correspond to SCE for the reference electrode. The surface of the working electrode was covered with epoxy resin to expose a test area of 0.6 cm². A platinum wire served as the counter electrode. Prior to potentiodynamic anodic polarization and potentiostatic polarization tests, the open circuit potential (OCP) was monitored and the experiments were begun after the stabilization of OCP for 1 hour. Furthermore, all the data were duplicated to ensure reproducibility of the results. Those experiments were carried out at a scan rate of 0.167 mV/s. After conducting the experiments, the morphology and distributed elements of the specimen surface were investigated and observed by using scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS).

## III. RESULT AND DISCUSSION

### A. Microstructure before polarization test

Fig. 1 shows microstructures of Ni₃(Si,Ti) +2Cr after the final polishing with galvanostatic etching process. It is found that Ni₃(Si,Ti) + 2Cr are composed of L1₂ phase (dark area) and (L1₂ + Ni_ss) mixture region (white area) as well as those phases in Ni₃(Si,Ti) with the addition of Al and Cr (Priyotomo et al.,2012). Furthermore, Kaneno and co-workers have already investigated and elucidated the microstructure and the phases of this compound in more detail (Kaneno et al., 2011).
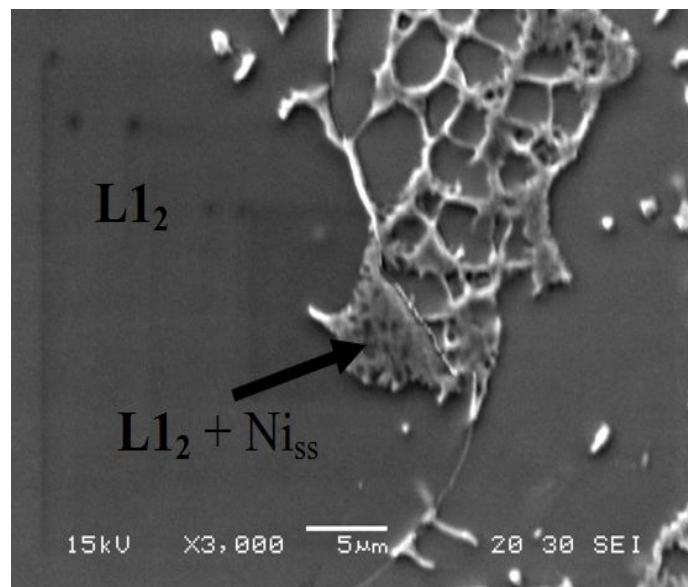


Fig. 1 Microstructure of Ni₃(Si,Ti)+2Cr before polarization test

*B. Determination of pitting potential (E_pit)*

Fig. 2 shows the potentiodynamic anodic polarization curves for $Ni_3(Si,Ti)$ + 2Cr intermetallic compounds in neutral sodium chloride solutions with various chloride concentrations at 293 K. The anodic current densities of these intermetallic compounds were very small up to a certain applied potentials, which referred to passive current densities. Furthermore, the anodic current density began to increase above a certain potential and suddenly increased with increasing applied potential. Fig. 3 shows a representative figure of a pit appearance for $Ni_3(Si,Ti)$ +2Cr after polarization test in 0.1 $kmol/m^3$ neutral sodium chloride solution at 293 K by applying scanning electron microscope (SEM) with secondary electron imaging method. The Fig 3 shows that the rapid rise in the anodic current density was caused by the initiation and propagation of the pit with an irregular shape. As shown in the inset figure of Fig. 2, the value of pitting potential (E_pit) was measured through the extrapolation of the increased anodic current density to the passive current density. On the other hand, the magnitude of the anodic current densities for $Ni_3(SiTi)$+2Cr and $Ni_3(Si,Ti)$ +4Al (Priyotomo et al.,2014) were more than one order higher compared to those for $Ni_3(Si,Ti)$ intermetallic compound (Priyotomo., 2013).
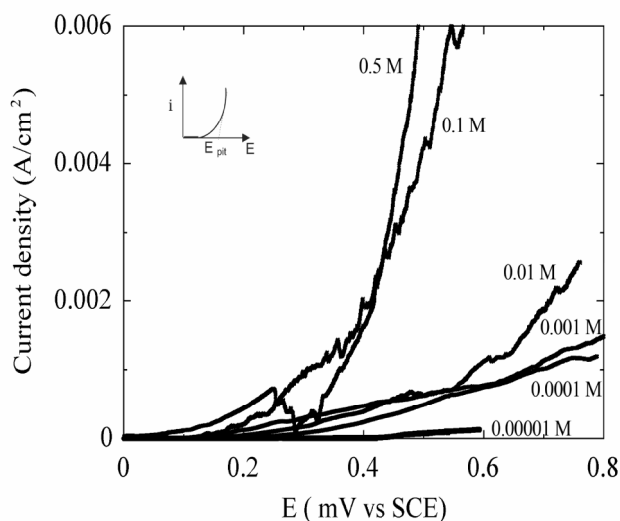


Fig.2. A potentiodynamic anodic polarization curves for $Ni_3(Si,Ti)$+2Cr intermetallic compounds with various chloride concentrations $(kmol/m^3)$ at 293 K.

In this work, no pit was found on the surface of $Ni_3(Si,Ti)$+2Cr at the chloride concentrations less than 0.0055 $kmol/m^3$ after the measurement of anodic polarization curves as well as the surface of $Ni_3(Si,Ti)$+4Al at the same condition (Priyotomo et al., 2014). Therefore, it was clearly found that no pitting corrosion took place at the chloride concentration less than 0.0055 $kmol/m^3$ as well as the $Ni_3(Si,Ti)$+4Al compound (Priyotomo et al., 2014). Furthermore, at a chloride concentration higher than 0.0055 $kmol/m^3$, the pitting potential was measured through the extrapolation method of the rapid increased anodic current density to the passive current density as shown in the figure inserted in Fig. 2, and an apparent pitting potential in the same method was also got at the

chloride concentrations less than 0.0055 $kmol/m^3$ with no occurrence of pitting corrosion (no pit) as well as $Ni_3(Si,Ti)$ + 4Al intermetallic compound in neutral NaCl solution (Priyotomo et al.,2014). In addition, Priyotomo had already found that no pits were found on the surfaces of type C-276 alloy and $Ni_3(Si,Ti)$ intermetallic compound at the chloride concentrations less than 0.05 $kmol/m^3$ and 0.01 $kmol/m^3$, respectively after measurement of anodic polarization curves, whereas at a chloride concentration higher than 0.05 $kmol/m^3$ for the surfaces of C276 alloy and 0.01 $kmol/m^3$ of $Ni_3(Si,Ti)$ intermetallic compound, pits were found clearly (Priyotomo.,2013).
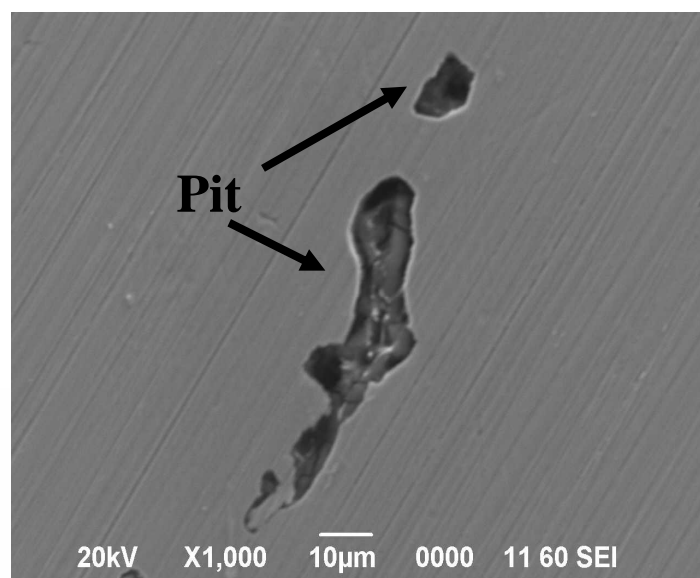


Fig. 3. A surface appearance of $Ni_3(Si,Ti)$+2Cr after polarization test in 0.1 $kmol/m^3$ neutral NaCl solution at 293 K.

*C. Effect of chloride concentration*

Fig. 4 shows the relationship between pitting potential (E_pit) and a logarithm of chloride concentrations for $Ni_3(Si,Ti)$ + 2Cr, $Ni_3(Si,Ti)$ + 4Al (Priyotomo et al.,2014), $Ni_3(Si,Ti)$ (Priyotomo., 2013) and C 276 alloy (Priyotomo., 2013) at 293 K. It was found that the pitting potential of $Ni_3(Si,Ti)$+2Cr increased linearly with decreasing chloride concentration up to a certain chloride concentration, below which no pitting corrosion occurred as well as the previous works such as $Ni_3(Si,Ti)$ compound, C 276 alloy (Priyotomo.,2013) and $Ni_3(Si,Ti)$+4Al compound (Priyotomo et al.,2014). Furthermore, the chloride concentration value at which no pitting corrosion occurred was defined as a critical chloride concentration ($Cl^-_{cri}$). The presence of the critical chloride concentration means that the parameters of film breakdown rate and repassivation rate are essential as well as the pitting corrosion of the homogenized $Ni_3(Si,Ti)$ compound (Wagle et al.,2011), $Ni_3(Si,Ti)$ compound after a thermomechanical treatment (Priyotomo et al.,2011) and $Ni_3(Si,Ti)$ +4Al compound after the thermomechanical treatment ( Priyotomo et al., 2014). Below the critical chloride concentration, the repassivation rate is superior to the film breakdown rate to show no occurrence of pitting corrosion process. Therefore, it implies that there is no defect on the surface of passive layer.
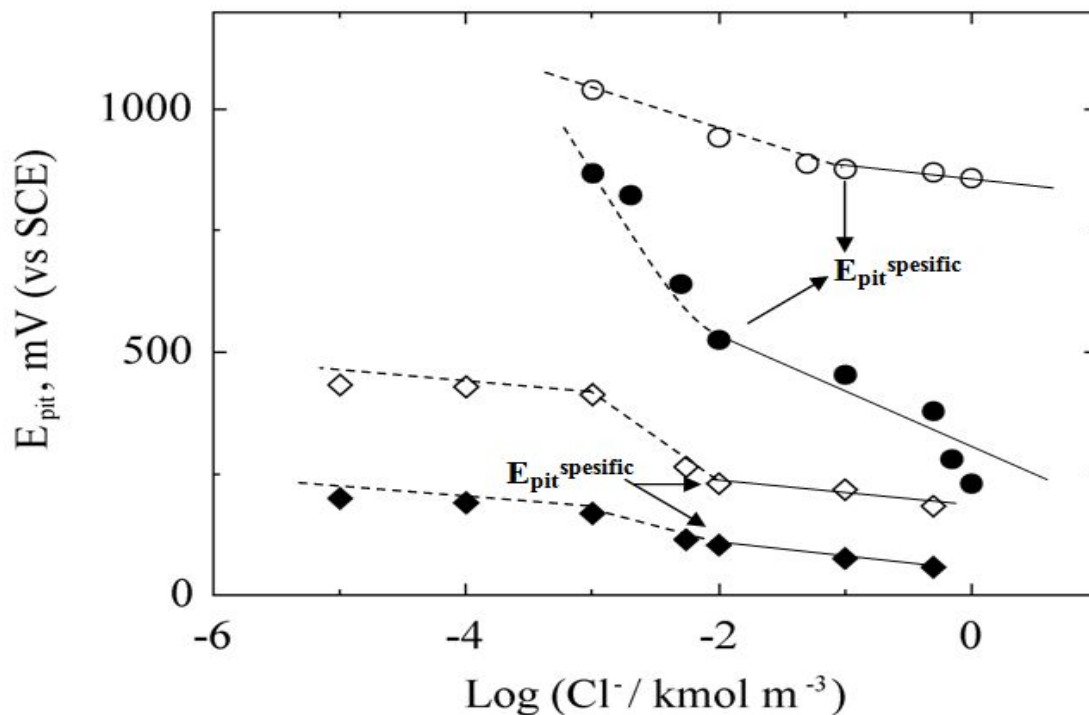
Fig.4 Chloride concentration dependence of pitting potential for ◇ Ni$_3$(Si,Ti) +2Cr ; ◆Ni$_3$(Si,Ti)+4Al (Priyotomo et al.,2014)[16]; ●Ni$_3$(Si,Ti) (Priyotomo., 2013)[8] and ○ C276 alloy (Priyotomo., 2013)[8] in neutral sodium chloride solutions at 293 K.

From Fig. 4, it was found that the pitting potential values of C276 alloy were the highest compared to among those of Ni$_3$(Si,Ti) without (Priyotomo et al., 2013) and with the addition of Al (Priyotomo et al., 2014) and Cr. This proof means that the pitting corrosion resistances were decreased in the order of C276 > Ni$_3$(Si,Ti) > Ni$_3$(Si,Ti) + 2Cr > Ni$_3$(Si,Ti) + 4Al in various chloride concentrations. Table 2 shows the relationship between a specific pitting potential ( E$_{pit}$specific ) and critical chloride concentration (Cl$^-_{cri}$), where the specific pitting potential is the pitting potential at the critical chloride concentration. From this table, it was found that the specific pitting potential were decreased in the order of C276 > Ni$_3$(Si,Ti) > Ni$_3$(Si,Ti) + 2Cr > Ni$_3$(Si,Ti) + 4Al, where pitting corrosion could not take place at a potential lower than E$_{pit}$Specific. Therefore, Ni$_3$(Si,Ti) + 2Cr has the moderate susceptibility of pitting corrosion compared to Ni$_3$(Si,Ti) and C276, where Ni$_3$(Si,Ti) + 4Al has the worst of pitting corrosion resistance due to the lowest critical chloride concentration.

Table 2. The relationship between the specific pitting potential (E$_{pit}$Specific) and critical chloride concentration (Cl$^-_{cri}$) on Ni$_3$(Si,Ti) with and without the addition of Al and Cr and C276 alloy in neutral sodium chloride solution at 293 K.

| Compounds | E$_{pit}$Specific (mV vs SCE) | Cl$^-_{cri}$ (kmol/m$^3$) |
|---|---|---|
| Ni$_3$(SI,Ti) + 2Cr | 264 | 0.0055 |
| Ni$_3$(Si,Ti)+4Al* | 114.3 | 0.0055 |
| Ni$_3$(Si,Ti)** | 530 | 0.01 |
| C276* | 889 | 0.05 |

*(Priyotomo., 2013) and **(Priyotomo et al.,2014)

D. Potentiostatic polarization measurement

Fig. 5 shows that the current densities of Ni$_3$(Si,Ti) +2Cr intermetallic compound recorded as a function of time for the different constant potential values such as -100 mV, +100 mV, +300 mV, +400 mV and +500 mV vs SCE in 0.1 kmol/m$^3$ neutral NaCl solution at 293 K for the immersion time of 4000 seconds. The current densities at -100mV and +100 mV vs SCE decrease with increasing the time and lies down in the passivity region which started from 50 seconds of time exposure as shown in Fig 6. Furthermore, the current densities as a function of immersion time rise rapidly at 500 seconds, when the various constant applied potentials were higher than the pitting potential (E$_{pit}$) in 0.1 kmol NaCl solution ( E$_{pit}$ : +217 mV vs SCE). On the other hand, by increasing the constant applied potentials above E$_{pit}$, the current densities increase up to 500 seconds indicating the presence of stable pitting occurred on the surface as well as austenitic stainless steel such as type 304 and type 316L (Ilevbare et al.,2001) and Ni$_3$(Si,Ti) + 4Al compound (Priyotomo et al, 2014). In addition, the stable propagation of pit was occurred in stable pitting with the growth of macropit (Williams et al.,1994). From 500 seconds of immersion time, at -100 mV and +100 mV vs SCE, the magnitude of current densities for Ni$_3$(Si,Ti)+2Cr were lower than those at +300 mV, 400 mV and +500 mV vs SCE, where at 100 mV and +100 mV vs SCE, the current densities of the compound became stable as function of time. Fig 6 shows that the current densities of Ni$_3$(Si,Ti) + 2Cr below E$_{pit}$ decrease with increasing the immersion time indicating the stable passive condition. Several peaks took place at the stable passive region corresponded to the metastable pit initiation of stainless steel (Ebrahimi et al.,2001).
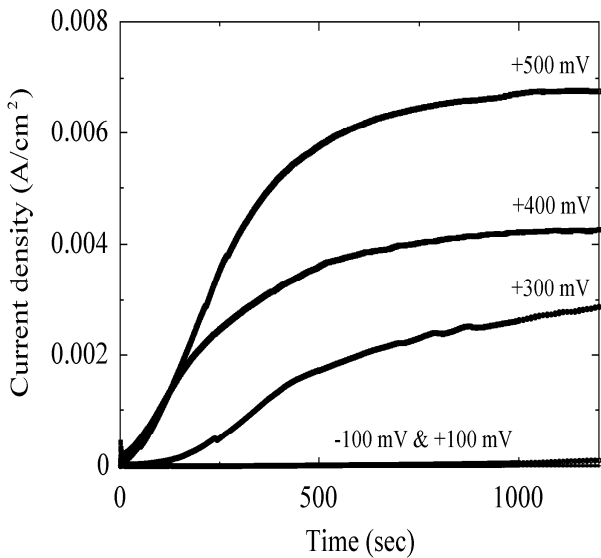
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Fig.5 Potentiostatic tests of Ni₃(Si,Ti)+2Cr at all constant potentials vs (SCE) as a function of immersion time in 0.1 kmol/m³ NaCl solution at 293 K
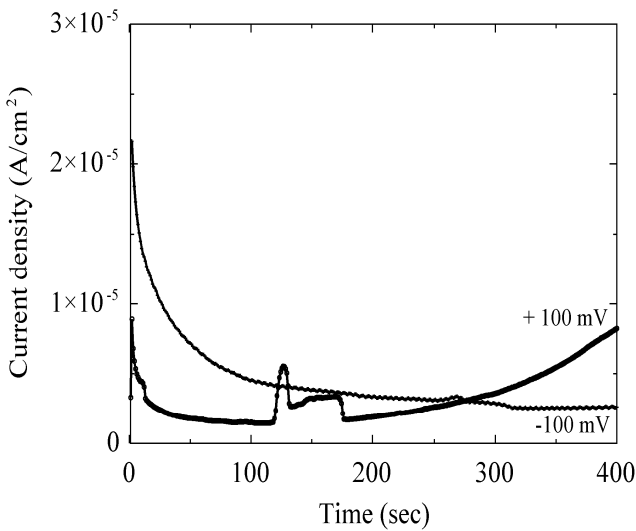


Fig.6 Potentiostatic tests of Ni₃(Si,Ti)+2Cr at constant potentials for +100 mV and -100mV vs (SCE) as a function of immersion time in 0.1 kmol/m³ solution at 293 K

*D. The effect of element distribution to the occurrence of pit*

Fig 7 shows the surface appearance of Ni₃(Si,Ti)+2Cr after potentiostatic polarization test in 0.1 kmol/m³ neutral NaCl solution at +300 mV vs SCE. It is difficult to observe the phases such as L1₂ + Ni_ss mixture phase and L1₂ phase containing the localized attack like pitting corrosion of this compound due to the small size of L1₂ +Ni_ss mixture phase. On the other hand, in Fig.8, by performing energy dispersive X-ray spectroscopy, the elements of Cr, Si, Ti and O was enriched in the edge or inside of pit, while the average amount of Ni distributed uniformly in the highest weight concentration outside pits. The presence of oxygen with high concentration level in the edge or inside of pit could be took place, where the hydrolysis process of the dissolved metal ion took place to produce free acid containing the cation of hydrogen inside pit and the hydroxide in adjacent pit (Trethewey et

al.,1988). Therefore, it implies that the presence of oxygen level in high concentration indicate the occurrence of pitting process.
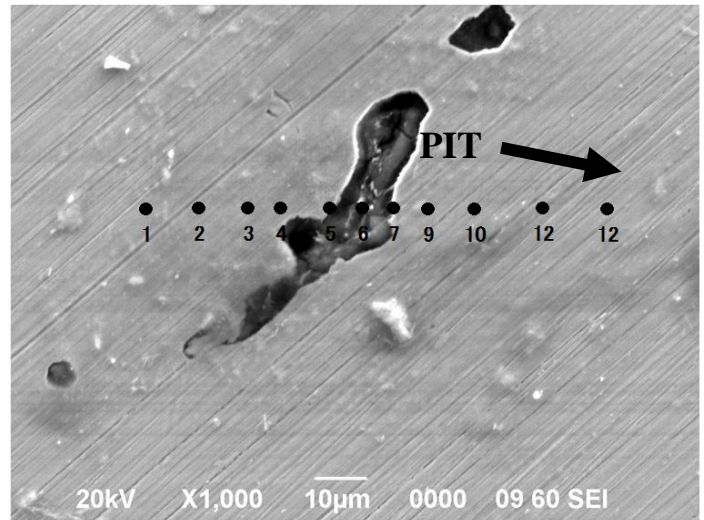


Fig. 7. The surface appearance of Ni₃(Si,Ti)+2Cr after the potentiostatic polarization test in 0.1 kmol/m³ neutral NaCl solution at constant potential of +300 mV vs SCE.



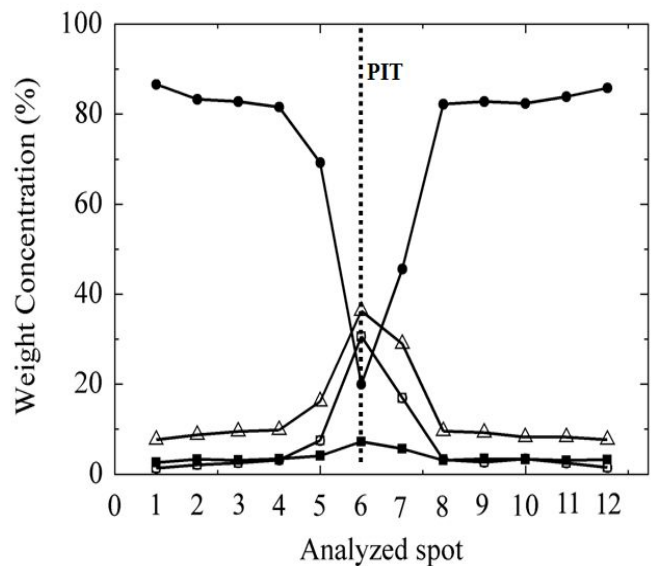Fig.8. Plot of the measured weight concentrations of ■Si, △Ti, ●Ni, ○Cr and □O for all spots analyzed on sample of Ni₃(Si,Ti) + 2Cr as shown in Fig.7.

## IV. CONCLUSION

The pitting corrosion behavior of Ni₃(Si,Ti)+2Cr intermetallic compound in various neutral sodium chloride solution has been investigated and compared with that of Ni₃(Si,Ti) with and without Al and C276 alloy. The following things were obtained as follows.

1. The pitting potential of Ni₃(Si,Ti) +2Cr decreased with increasing chloride concentration above the critical chloride concentration, below which no pitting corrosion took place as well as those of Ni₃(Si,Ti) with and without Al and C276 alloy.
2. The specific pitting potentials and the pitting potentials were decreased in the order of C276 alloy > Ni₃(Si,Ti) > Ni₃(Si,Ti) + 2Cr > Ni₃(Si,Ti) + 4Al

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3. The pitting corrosion resistances were decreased in the order of C276 alloy > $Ni_3(Si,Ti)$ > $Ni_3(Si,Ti)$ + 2Cr > $Ni_3(Si,Ti)$ + 4Al in various chloride concentrations.
4. The presence of oxygen level in high concentration indicates the occurrence of pit.

## REFERENCES

1. Colin, J., Serna, S., Campillo, B., Florez, O. And Gonzalez-Rodriguez, J.G.(2007). Corrosion Performance of a Rapidly Solidified NiAl Intermetallic Macroallolled with Fe in 0.5M $H_2SO_4$. INTERNATIONAL JOURNAL OF ELECTROCHEMICAL SCIENCE, **2** : 947-957.
2. Ebrahimi, N., Moayed, M.H and Davoodi, A. 2011. Critical Pitting Temperature Dependence of 2205 Duplex Stainless Steel on Dichromate Ion Concentration in Chloride Medium. Corrosion Science 53:1278-1287
3. Fujimoto, Y., Kaneno, Y., Yoshida, M., and Takasugi, T. (2011). Alloy design for Al addition on microstructure and mechanical properties of $Ni_3(Si,Ti)$ alloy. *MATERIALS SCIENCE AND ENGINEERING* A 528 : 4104–4110.
4. Ilevbare, G.O. and Burstein,G.T.(2001). The role of alloyed molybdenum in the inhibition of pitting corrosion in stainless steels. *CORROSION SCIENCE 43*: 485-513.
5. Kaneno,Y., Fujimoto, Y., Yoshida, M. And Takasugi, T. (2011). Alloying Effect on Microstruture and Mechanical Properties of Thermomechanical Processed $Ni_3(Si,Ti)$ Alloys. *INTERNATIONAL JOURNAL OF MATERIALS RESEARCH*, **102(5)**: 1-7.
6. Priyotomo, G., Okitsu, K., Iwase, A., Kaneno, Y., Nishimura, R. and Takasugi, T. (2011). The corrosion behavior of intermetallic compounds Ni3(Si,Ti) and Ni3(Si,Ti) + 2Mo in acidic solutions. *APPLIED SURFACE SCIENCE*, **257(19)**: 8268-8274.
7. Priyotomo, G., Wagle, S., Okitsu, K., Iwase, A., Kaneno, Y., Nishimura, R. and Takasugi, T. (2012). The corrosion behavior of $Ni_3(Si,Ti)$ intermetallic compounds with Al, Cr, and Mo in various acidic solutions. *CORROSION SCIENCE*, **60**: 10-17.
8. Priyotomo, G. (2013). Pitting Corrosion of $Ni_3(Si,Ti)$ Intermetallic Compound at Various Chloride Concentrations. *INTERNATIONAL JOURNAL OF SCIENCE AND ENGINEERING.* **Vol.5 (2)** : 25-28.
9. Priyotomo, G., Sebleku, P. and Kaneno, Y. (2014). Pitting Corrosion of $Ni_3(SI,Ti)$ +4Al Intermetallic Compound at Various Chloride Concentrations. *INTERNATIONAL JOURNAL OF SCIENCE AND ENGINEERING* 6(2)
10. Takasugi, T., Nakayama, T. and Hanada, S.(1993a). Environmental embrittlement of $Ni_3(Si, Ti)$ single crystals. *MATERIALS TRANSACTIONS JIM*, **34(9)**:775-785. ISSN: 09161821.
11. Takasugi, T., Hono, K., Suzuki, S., Hanada, S. and Sakurai, T.(1993b). Environmental embrittlement and grain boundary segregation of boron in $Ni_3(Si,Ti)$ and $Co_3Ti$ alloys. *SCRIPTA METALLURGICA ET MATERIALA*, **29(12)**: 1587-1591. ISSN: 0956716X.
12. Trethewey,K.R., and Chamberlain, J.,(1988). Corrosion for Students of science and engineering. Longman Sc & Tech,United Kingdom. ISBN: 978-0470207949, pp:144.
13. Wagle, S., Priyotomo, G., Kaneno, Y., Iwase, A., Takasugi, T. and Nishimura, R.(2011a). Pitting Corrosion of Intermetallic Compound $Ni_3(Si,Ti)$ in Sodium Chloride Solutions. *CORROSION SCIENCES*, **53**: 2514-2517.
14. Wagle, S., Priyotomo, G., Kaneno, Y., Iwase, A., Takasugi, T. and Nishimura, R.(2011b). Pitting Corrosion of Intermetallic Compound $Ni_3(Si,Ti)$ with 2 at% Mo in Sodium Chloride Solutions. *CORROSION SCIENCES*, **55**: 140-144.
15. Williams, D., Stewart, J and Balkwill, P.H. (1994). The Nucleation, Growth and Stability of Micropits in Stainless Steel. *CORROSION SCIENCE* **36 (7)**:1213-1235.

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