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Pitting Corrosion of $\text{Ni}_3(\text{Si,Ti})+4\text{Al}$ 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*

¹gadangp@gmail.com

**Department of Materials Science, Graduate School of Engineering, Osaka Prefecture University
1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan*

²kaneno@mtr.osakafu-u.ac.jp

Abstract - The pitting corrosion of $\text{Ni}_3(\text{Si,Ti})$ with 4 at% Al consisting of two regions of a $\text{Ni}_3(\text{Si,Ti})$ single-phase of L_{12} structure and two phases of L_{12} and fcc Ni_{ss} was investigated as function of chloride concentrations by using electrochemical method, scanning electron microscope and energy dispersive X-Ray spectroscopy in neutral sodium chloride solutions at 293 K. In addition, the pitting corrosion of $\text{Ni}_3(\text{Si,Ti})$ and type C276 alloy were also studied under the same experimental condition for comparison. The pitting potential obtained for the $\text{Ni}_3(\text{Si,Ti})$ with 4 at%Al decreased with increasing chloride concentration. The specific pitting potential and pitting potential of $\text{Ni}_3(\text{Si,Ti})$ with 4 at%, $\text{Ni}_3(\text{Si,Ti})$ and C276 were the lowest, the moderate and the highest, respectively, which means that the pitting corrosion resistance of $\text{Ni}_3(\text{Si,Ti})$ was higher than $\text{Ni}_3(\text{Si,Ti})$ with 4 at% Al, but lower than that of C276. A critical chloride concentration of $\text{Ni}_3(\text{Si,Ti})$ with 4 at% Al was found to be lower than that of $\text{Ni}_3(\text{Si,Ti})$. The Pitting corrosion of $\text{Ni}_3(\text{Si,Ti})$ with 4 at% Al occurred in the two phase mixture ($L_{12} + \text{Ni}_{ss}$).

Keywords : Intermetallic compound; Pitting Corrosion; Sodium Chloride; Polarization

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I. INTRODUCTION

The nickel base intermetallic compounds such as $\text{Ni}_3(\text{Si,Ti})$ with and without addition of Al, 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 ; Kawahara et al., 2009). Therefore, those intermetallic compounds are as a candidate compound which could be used as high-temperature materials and chemical parts (Takasugi et al., 2002). On the other hand, an improvement in the mechanical property of the $\text{Ni}_3(\text{Si,Ti})$ intermetallic compound was attempted with macro-alloying by adding aluminium (Al), which enhanced high-temperature tensile elongation at various operational temperatures (Kaneno et al.,2011). Furthermore, the addition of Al in $\text{Ni}_3(\text{Si,Ti})$ also improved the oxidation resistance at elevated operational temperatures (Kaneno et al.,2011). The $\text{Ni}_3(\text{Si,Ti})$ with 4 at.% Al were composed of two regions of the L_{12} single-phase and a two phase mixture of L_{12} and

Ni_{ss} , where Ni_{ss} was a fcc Ni solid solution (Kaneno et al., 2011). Before performing electrochemical test, Gadang and co-workers also found that the main element of Ni was present uniformly, whereas Al, Ti and Si were enriched in the L_{12} single-phase region (Priyotomo et al., 2002). Thus, Al was found to be enriched in the L_{12} single-phase region, not like Mo in the two phase region $L_{12} + \text{Ni}_{ss}$ (Priyotomo et al., 2011). In addition, the $\text{Ni}_3(\text{Si,Ti})$ intermetallic compounds are susceptible to environmental embrittlement (hydrogen embrittlement) at ambient temperature in moist environment (Takasugi et al.,1993a,b), where that embrittlement takes place with permeation of atomic hydrogen through electrochemical reaction into the compounds.

Up to the present, the intermetallic compound such as $\text{Ni}_3(\text{Si,Ti})$ with the addition of Al have not systematically been investigated for pitting corrosion in aqueous solution. On the other hand, the pitting corrosion behavior of $\text{Ni}_3(\text{Si,Ti})$ with and without addition of Mo in the different heat treatment already were

investigated in aqueous solution (Wagle et al., 2011a,b ; Priyotomo., 2013). Therefore, the purpose this work is to elucidate the pitting corrosion behavior of Ni₃(Si,Ti) with addition of 4 at % Al with various chloride concentrations at 293 K and to compare with that of Ni₃(Si,Ti) intermetallic compound and C-276 alloy as the references (Priyotomo., 2013).

II. EXPERIMENTAL

A. The specimens

Ni-11 at.% Si- 5.5 at.% Ti-4 at.% Al compound with the addition of 50 wt. ppm (part per million) of boron was prepared by using an arc melting method under an argon gas atmosphere in a 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. Type of C276 alloy and Ni₃(Si,Ti) intermetallic compound also was as the references for the experiments (Priyotomo et al.,2013). The chemical and nominal compositions of materials are given in Table 1.

Table 1: Composition and nominal of the materials investigated

Elements	Ni ₃ (Si,Ti)+4Al	Ni ₃ (Si,Ti)*	C276*
	At%		
C	-	-	0.02
Si	11.0	11.0	0.08
Mn	-	-	1.00
P	-	-	0.03
S	-	-	0.03
Ni	79.5	79.5	50.99
Cr	-	-	16.5
Mo	4-	-	17
V	-	-	0.35
Fe	-	-	7
Ti	5.5	9.5	-
W	-	-	4.5
Co	-	-	2.5
Al	4.0	-	-
ppm			
B	50		-

* (Priyotomo.,2013)

B. Electrochemical test

The specimens were polished with emery paper to 1000 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 prepared with the distilled water and high grade chemical reagent. The test temperatures used was 293 K. The electrochemical experiments were conducted in a round bottom cell of 1000 ml capacity using a potentiostat instrument (Reference 600,Gamry Instrument), interfaced to a personal computer. The potential values were monitored using a saturated calomel electrode (SCE). All potentials referred in this present work are with respect to SCE. The surface of the working electrode was covered with resin to expose an effective area of 0.6 cm². A platinum wire served as the counter electrode. Prior to potentiodynamic anodic polarization and potentiostatic polarization test, the open

circuit potential (OCP) was monitored and the experiments were begun after stabilization of OCP for 1 hour. Furthermore, all the results were duplicated so as to ensure reproducibility of the results. Those experiments were conducted at a scan rate of 0.167 mV/s. After conducting the experiments, the morphology and distributed elements of the specimen surface was investigated by using scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS).

III. RESULT AND DICUSSION

A. Microstructure before electrochemical test

Fig. 1 shows microstructures of Ni₃(Si,Ti) +4Al after the final polishing. It is clearly found that Ni₃(Si,Ti) + 4Al are composed of L₁₂ phase (dark area) and (L₁₂ + Ni_{ss}) mixture region (light area). Furthermore, Kaneno and co-workers have already investigated the microstructure and the phases of this compound in detail (Kaneno et al.,2011).

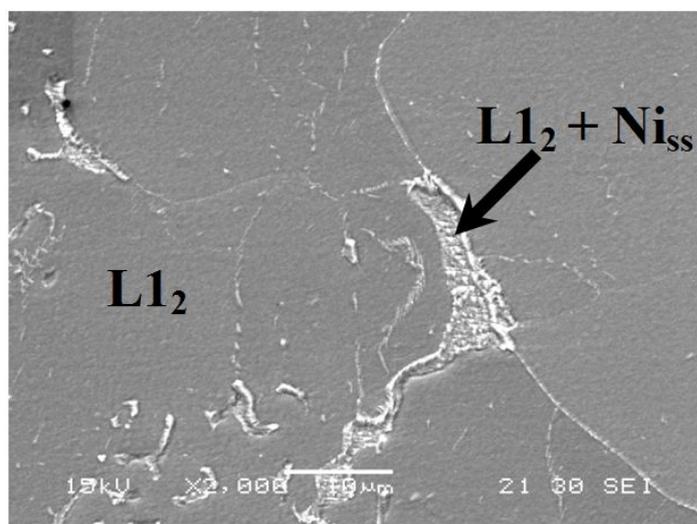


Fig. 1 Microstructure of Ni₃(Si,Ti)+4Al before electro chemical test.

B. Determination of pitting potential (E_{pit})

Fig. 2 shows the representative of potentiodynamic anodic polarization curves for Ni₃(Si,Ti) + 4Al in neutral sodium chloride solutions with various chloride concentrations at 293 K. The anodic current densities of these intermetallic compounds were negligibly small up to a certain applied potential, which related to a passive current density. Furthermore, the anodic current density started to increase above a certain potential and increased rapidly with increasing applied potential. Fig. 3 shows an representative figure of a pit appearance for Ni₃(Si,Ti) +4Al after conducting electrochemical test in 0.1 kmol/m³ neutral sodium chloride solution at 293 K by using scanning electron microscope (SEM). This evidence shows that the rapid rise in anodic current density is caused by the formation of the pit with an average size of 70 m. As shown in the inset figure in Fig. 2, pitting potential (E_{pit}) was determined through the extrapolation of the increased anodic current density to the passive current density. In addition, the magnitude of

the anodic current density for this compound was more than one order higher compared to those for $\text{Ni}_3(\text{Si,Ti})$ intermetallic compound and C 276 (Priyotomo., 2013).

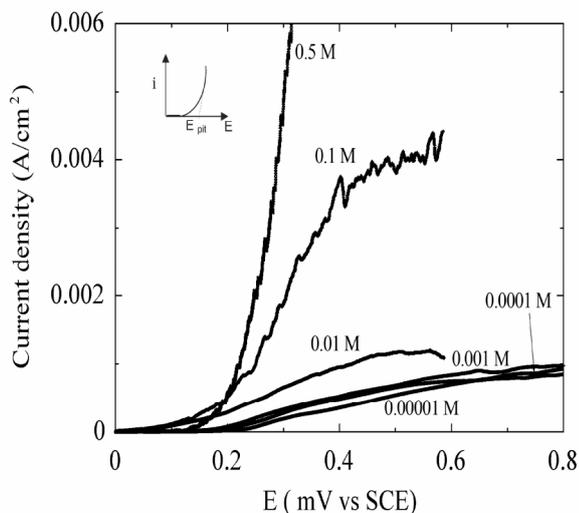


Fig.2. A representative of potentiodynamic anodic polarization curves for $\text{Ni}_3(\text{Si,Ti})+4\text{Al}$ with various chloride concentrations (kmol/m^3) at 293 K.

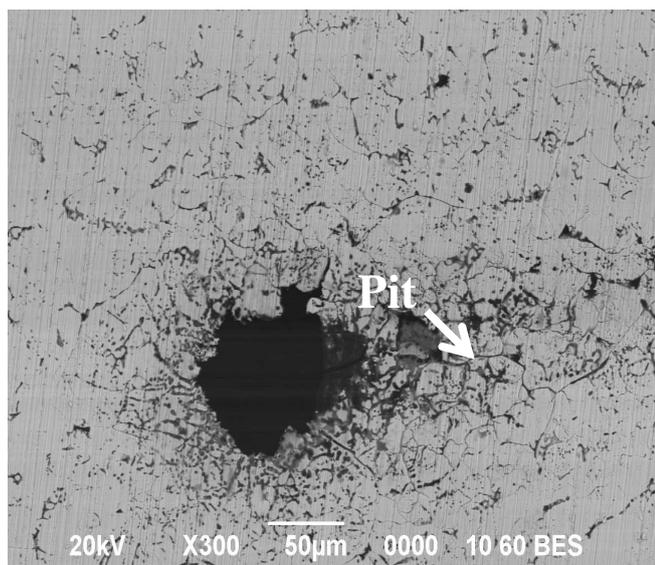


Fig. 3. A corroded surface appearance of $\text{Ni}_3(\text{Si,Ti})+4\text{Al}$ after electrochemical test in 0.1 kmol/m^3 neutral NaCl solution at 293 K.

Furthermore, in the present work, no pit was observed on the surface of $\text{Ni}_3(\text{Si,Ti})+4\text{Al}$ at the chloride concentrations less than 0.0055 kmol/m^3 after measurement of anodic polarization curves. Therefore, it was found that no pitting corrosion took place at the chloride concentration less than 0.0055 kmol/m^3 . At a chloride concentration higher than 0.0055 kmol/m^3 , the pitting potential was determined through the extrapolation of the 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 manner was also obtained at the chloride concentrations less than 0.0055 kmol/m^3 with no occurrence of pitting corrosion (no pits) as well as

$\text{Ni}_3(\text{Si,Ti})$ intermetallic compound in neutral NaCl solution (Priyotomo.,2013). On the other hand, Priyotomo had already found that no pits were observed on the surfaces of type C-276 and $\text{Ni}_3(\text{Si,Ti})$ 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 C276 and 0.01 kmol/m^3 for $\text{Ni}_3(\text{Si,Ti})$, pits were observed (Priyotomo.,2013).

C. Effect of chloride concentration

Fig. 4 shows the relationship between pitting potential (E_{pit}) and a logarithm of chloride concentrations for $\text{Ni}_3(\text{Si,Ti}) + 4\text{Al}$, $\text{Ni}_3(\text{Si,Ti})$ and C 276 alloy at 293 K. It was found that pitting potential of $\text{Ni}_3(\text{Si,Ti})+4\text{Al}$ increased linearly with decreasing chloride concentration up to a certain chloride concentration, below which no pitting corrosion took place as well as a previous work ($\text{Ni}_3(\text{Si,Ti})$ and C 276 alloy (Priyotomo.,2013). The chloride concentration at which no pitting corrosion took place was defined as a critical chloride concentration (Cl^-_{cri}) as shown in the Fig. 4. The presence of the critical chloride concentration means that the parameters of film breakdown rate and repassivation rate are important as well as the pitting corrosion of the homogenized $\text{Ni}_3(\text{Si,Ti})$ (Wagle.,2011) and $\text{Ni}_3(\text{Si,Ti})$ after thermomechanical treatment (Priyotomo.,2011). Below the critical chloride concentration, the repassivation rate is dominant to the film breakdown rate to show no occurrence of pitting corrosion.

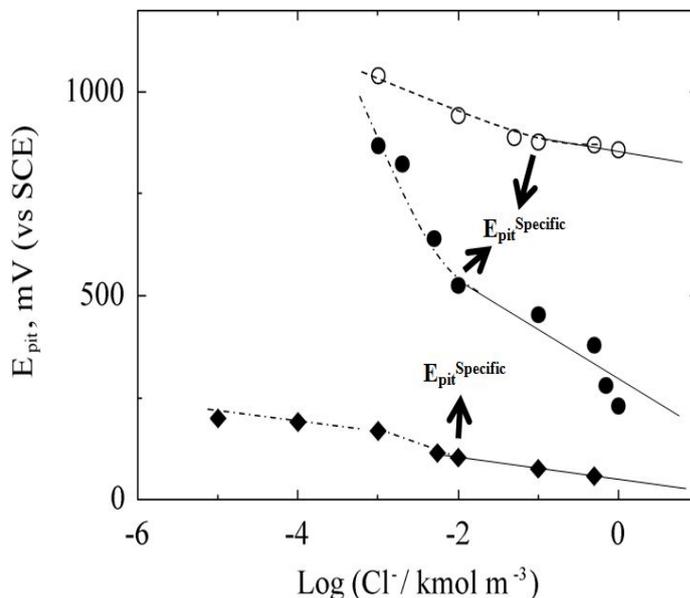


Fig.4 Chloride concentration dependence of pitting potential for $\blacklozenge \text{Ni}_3(\text{Si,Ti}) + 4\text{Al}$; $\bullet \text{Ni}_3(\text{Si,Ti})$ (Priyotomo.,2013) and \circ C276 alloy (Priyotomo.,2013) in neutral sodium chloride solutions at 293 K.

From Fig. 4, it was also found that pitting potential of C276 was the highest compared to both those of $\text{Ni}_3(\text{Si,Ti})$ with and without the addition of Al. This means that $\text{Ni}_3(\text{Si,Ti}) + 4\text{Al}$, $\text{Ni}_3(\text{Si,Ti})$ and C276 have the lowest, the moderate, and the highest pitting corrosion resistances,

respectively. Furthermore, 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 Table 2, it was found that the specific pitting potential of $Ni_3(Si,Ti)+4Al$ was the lowest than that of both material references, where pitting corrosion could not take place at a potential lower than $E_{pit}^{specific}$. Therefore, $Ni_3(Si,Ti) + 4Al$ has the susceptibility of pitting corrosion compared to $Ni_3(Si,Ti)$ and C276 due to the lowest $E_{pit}^{specific}$ of $Ni_3(Si,Ti) + 4Al$ at the lowest critical chloride concentration.

Table 2. The relationship between the specific pitting potential ($E_{pit}^{specific}$) and critical chloride concentration (Cl_{cri}) in neutral sodium chloride solution at 293 K.

Compounds	$E_{pit}^{specific}$ (mV vs SCE)	Cl_{cri} (kmol/m ³)
$Ni_3(Si,Ti)+4Al$	114.3	0.0055
$Ni_3(Si,Ti)^*$	530	0.01
C276*	889	0.05

*(Priyotomo., 2013)

D. Potentiostatic polarization measurement

Fig. 5 shows that current densities of $Ni_3(Si,Ti) + 4Al$ intermetallic compound recorded as a function of time for different constant potential values such as -100 mV, +100 mV, +300 mV, +400 mV and +500 mV vs (SCE) in 0.1 kmol/m³ NaCl solution at 293 K for 4000 sec.

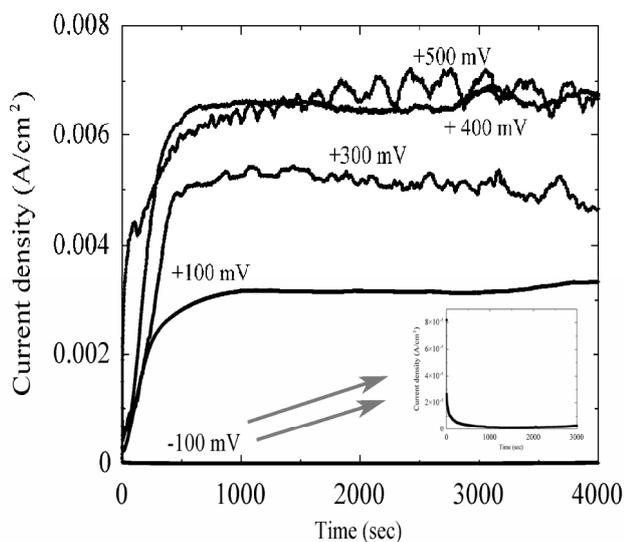


Fig. 5 Potentiostatic tests of $Ni_3(Si,Ti)+4Al$ at constant potentials vs (SCE) in 0.1M NaCl solution at 293 K

The current density at -100mV vs SCE decreases within the time and lies down in the passivity region which started from 1000 sec of time exposure (the inserted graph). On the other hand, the behavior of current density as a function of time changed drastically, when a constant various applied potential was higher than pitting potential (E_{pit}) in 0.1 kmol NaCl solution ($E_{pit} : +75$ mV vs SCE). Furthermore, by increasing constant applied potentials above E_{pit} , the current densities increase up to 500 sec 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). In addition, the stable propagation of pit was take place in stable pitting with the growth of macropit (Williams et al.,1994), where Fig.2 shows macropit with 70 micron meter of size. Furthermore, from 500 sec of exposure time, at +100 mV vs SCE, current density of $Ni_3(Si,Ti)+4Al$ became stable as function of time, whereas those became fluctuations at +300 mV, 400mV and +500 mV vs SCE. The intensity of current fluctuation for this compound increases with increasing applied potential. In addition, the higher intensity of current fluctuation can be indicated a localized attack like pitting and preferential corrosion (Colin et al., 2007).

E. The effect of element distribution to the occurrence of pit

Fig 6 shows a corroded surface appearance of $Ni_3(Si,Ti)+4Al$ after potentiostatic polarization test in 0.1 kmol/m³ neutral NaCl solution at +500 mV vs SCE. The localized attack like pitting corrosion of this compound took place in $L1_2 + Ni_{ss}$ mixture phase, but not in $L1_2$ phase.

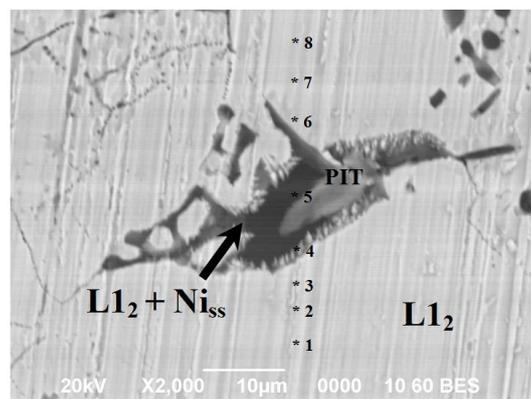


Fig. 6. Surface appearance of $Ni_3(Si,Ti)+4Al$ after potentiostatic polarization test in 0.1 kmol/m³ neutral NaCl solution at +500 mV vs SCE.

On the other hand, in Fig.7, by performing energy dispersive X-ray spectroscopy, the elements of Al, Si and Ti was enriched in $L1_2$ phase, while the average amount of Ni distributed uniformly in the highest weight concentration. In addition, the less enrichment of Al was distributed in $L1_2 + Ni_{ss}$ phase compared to $L1_2$ phase as well as the result of previous paper in acidic solutions (Priyotomo.,2012). The presence of oxygen with high concentration in the edge of pit could be resulted, where the hydrolysis of the dissolved metal ion took place to produce free acid inside pit and the hydroxide in adjacent pit. Therefore, the amount of oxygen level could be detected from EDS with the presence of hydroxide.

Furthermore, from the present result, it was found that the addition of Al to $Ni_3(Si,Ti)$ intermetallic compound showed a detrimental effect on improvement of the pitting corrosion resistance of $Ni_3(Si,Ti)$ in neutral NaCl solution. The main cause may come from two following things: (1). The different two regions of phase ($L1_2$ and ($L1_2 + Ni_{ss}$)) showed the different distribution of the elements and (2). The depletion of Al in the $L1_2 +$

Niss phase compared with in L12 phase. On the other hand, the presence of Si and Ti increase corrosion resistance as has been revealed by comparison of ternary Ni₃(Si,Ti) and pure Ni (Wagle et al.,2011). The contents of Si and Ti in the (L12 and Niss) mixture region are lower than those in the L12 single-phase region, and the presence of Al is not effective in enhancing the pitting corrosion resistance at certain potential, where pitting occurs. Consequently, pitting corrosion was found selectively in the (L12 and Niss) mixture region, but not in the L12 phase.

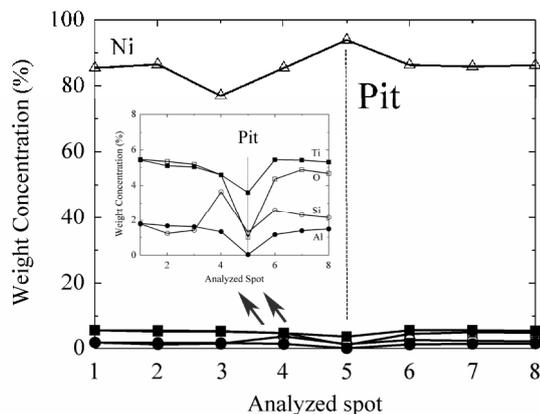


Fig.7. Plot of the measured weight concentrations of Si, Ti, Ni, Al and O for all spots analyzed on sample of Ni₃(Si,Ti) + 4Al as shown in Fig.6.

V. CONCLUSION

The pitting corrosion behavior of Ni₃(Si,Ti)+4Al intermetallic compound in various neutral sodium chloride solution has been studied and compared with that of Ni₃(Si,Ti) compound and C276 alloy. The following things were obtained as follows.

1. The pitting potential of Ni₃(Si,Ti) +4Al 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) and C276 alloy.
2. The pitting potentials and the specific pitting potentials of Ni₃(Si,Ti) +4Al, Ni₃(Si,Ti) and C276 alloys were the lowest, the moderate and the highest, respectively.
3. The pitting corrosion resistances of Ni₃(Si,Ti)+4Al and C276 alloys were the lowest and the highest, respectively.

4. The pit was formed in the two phase mixture region of (L1₂ + Ni_{ss}).

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