



# International Journal of Science and Engineering (IJSE)

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## Pitting Corrosion of $\text{Ni}_3(\text{Si},\text{Ti})$ Intermetallic Compound at Various Chloride Concentrations

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**Abstract** - The pitting corrosion of  $\text{Ni}_3(\text{Si},\text{Ti})$  intermetallic compound was investigated as function of chloride concentration by using electrochemical method and scanning electron microscope in sodium chloride solutions at 293 K. In addition, the pitting corrosion of type C276 alloy was also studied under the same experimental condition for comparison. The pitting potential obtained for the intermetallic compound decreased with increasing chloride concentration. The specific pitting potential and pitting potential of  $\text{Ni}_3(\text{Si},\text{Ti})$  were lower than those of C276 alloy, which means that the pitting corrosion resistance of C276 alloy was higher than that of  $\text{Ni}_3(\text{Si},\text{Ti})$ .

**Keywords** — Anodic Polarization Curve, Pitting Corrosion, Intermetallics, Chloride

Submission: July 26, 2013

Corrected : August 12, 2013

Accepted: September 20, 2013

Doi: [10.12777/ijse.5.2.25-28](https://doi.org/10.12777/ijse.5.2.25-28)

[How to cite this article: Priyotomo, G. (2013). Pitting Corrosion of  $\text{Ni}_3(\text{Si},\text{Ti})$  Intermetallic Compound at Various Chloride Concentrations. *International Journal of Science and Engineering*, 5(2),18-24. Doi: [10.12777/ijse.5.2.25-28](https://doi.org/10.12777/ijse.5.2.25-28)]

### I. INTRODUCTION

$\text{Ni}_3(\text{Si},\text{Ti})$  intermetallic compounds with  $\text{L}_{12}$  structure have unique strength and ductility properties; that is, (1) an increase in flow strength with increasing temperature and (2) high ductility over a wide range of test temperature (Takasugi et al., 1990 ; Takasugi et al., 1991). In particular, their strength level were extremely high compared to those of other  $\text{L}_{12}$  ordered intermetallic compounds which have been developed as advanced materials (Kaneno et al., 2008). On the other hand,  $\text{Ni}_3(\text{Si},\text{Ti})$  intermetallic compounds have superior mechanical properties compared to those of conventional alloys such as nickel -base alloys, steel and stainless steel. In addition, this compound was shown an excellent oxidation resistance in air at ambient and elevated temperatures (Kaneno et al., 2007). On the other hand, the compounds have shown to be susceptible to environmental embrittlement (specifically hydrogen embrittlement) at ambient temperature in moisture in air and hydrogen gas (Kaneno et al.,2011 ; Takasugi et al., 1993a ; Takasugi et al., 1993b). The addition of boron of  $\text{Ni}_3(\text{Si},\text{Ti})$  was to suppress environmental embrittlement (Takasugi et al., 1995), although the intergranular attack were observed for this as-homogenized  $\text{Ni}_3(\text{Si},\text{Ti})$  compound (Priyotomo et al.,2011) and  $\text{Ni}_3(\text{Si},\text{Ti})$  compound after thermomechanical process (Priyotomo et al.,2013) in acidic solutions, which

took place by boron segregation at grain boundaries.

However, with regard to  $\text{Ni}_3(\text{Si},\text{Ti})$  intermetallic compounds after thermomechanical process, there is little study on their pitting corrosion in sodium chloride solutions at 293 K, although the pitting corrosion behavior of as-homogenized  $\text{Ni}_3(\text{Si},\text{Ti})$  compounds were qualitatively investigated in chloride ion solutions (Wagle et al.,2011a). Therefore, the purpose of this work is to elucidate the pitting corrosion behavior of  $\text{Ni}_3(\text{Si},\text{Ti})$  after thermomechanical process with various chloride concentration at 293 K and to compare with that of C276 alloy.

### II. EXPERIMENTAL

#### A. The specimens

Ni-11 at.% Si-9.5 at.% Ti compound with the addition of 50 wt. ppm of boron, which was known to form an ordered  $\text{L}_{12}$  single phase of  $\text{Ni}_3(\text{Si},\text{Ti})$ , was prepared by using an arc melting method under an argon gas atmosphere. It was homogenized at 1323K for 48 h under argon atmosphere and then cooled in vacuum furnace with cooling rate of 283 K/ min. Homogenized ingot was conducted a warm rolling at 573 K in air until obtaining the desired thickness and then a cold rolling until 1.2 mm of thickness in 75 % reduction. After obtaining cold-rolled thin sheet, this sheet was finally annealed from 873K to

1273K for 1 h. Type of C276 alloy also was as the reference for the experiments. The chemical and nominal compositions of materials are given in Table 1.

Table 1: Composition and nominal of the materials investigated

Elements	Ni <sub>3</sub> (Si,Ti) C-276	
	At%	
C	-	0.52
Si	11.0	0.11
Mn	-	1.14
P	-	0.0081
S	-	0.058
Ni	79.5	57.95
Cr	-	19.21
Mo	-	10.41
V	-	0.37
Fe	-	6.15
Ti	9.5	-
W	-	4.5
Co	-	2.65
Part per million (ppm)		
B	50	-

**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 sodium chloride solutions with various chloride concentrations (0.001 to 1 kmol/m<sup>3</sup>), which were prepared with the distilled water and guaranteed grade chemical reagent. The test temperatures used was 293 K.

Electrochemical experiments were performed in a round bottom cell of 1000 ml capacity using a potentiostat (Reference 600,Gamry Instrument), interfaced to a personal computer. The potential was monitored using a saturated calomel electrode (SCE). All the potentials referred in this work are with respect to SCE. The surface of the working electrode was covered with resin to expose an effective area of 1.4 cm<sup>2</sup>. A platinum wire served as the counter electrode. Prior to anodic polarization test, the open circuit potential (OCP) was monitored and experiments were begun after stabilization of OCP. All the results were duplicated so as to ensure reproducibility of the test results. Those experiments were conducted at a scan rate of 0.167 mV/s. After the experiments, the morphology of the specimen surface was investigated by using scanning electron microscope (SEM).

**III. RESULTS AND DISCUSSION**

**A Determination of pitting potential (E<sub>pit</sub>)**

Fig. 1 shows the representative of the anodic polarization curves for Ni<sub>3</sub>(Si,Ti) in sodium chloride solutions with various chloride concentrations at 293 K. The anodic current densities of the 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.

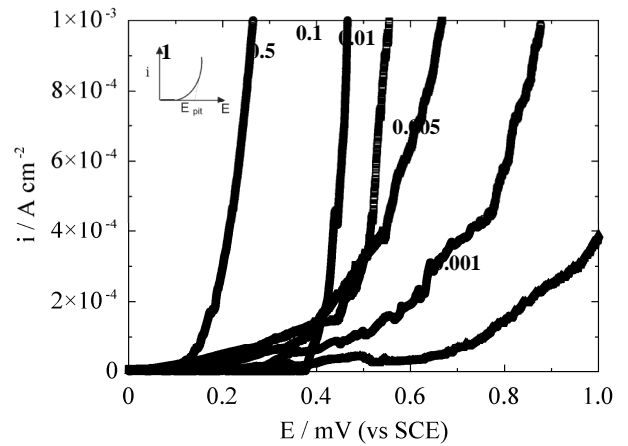


Fig.1. Anodic polarization curves for Ni<sub>3</sub>(Si,Ti) with various chloride concentrations (kmol/m<sup>3</sup>) at 293 K.

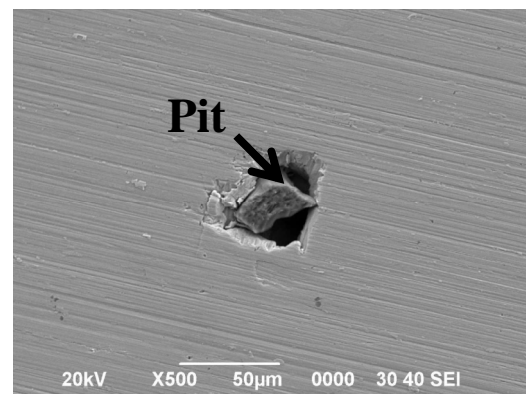


Fig. 2. Surface appearance of Ni<sub>3</sub>(Si,Ti) after experiment in 0.1 kmol/m<sup>3</sup> NaCl solution at 293 K.

Fig. 2 shows an example of a pit appearance for Ni<sub>3</sub>(Si,Ti) after the experiment in 0.1 kmol/m<sup>3</sup> sodium chloride solution at 293 K by using scanning electron microscope. This evidences shows that the rapid rise in anodic current density caused by the formation of the pit. As shown in the inset figure in Fig. 1, pitting potential ( E<sub>pit</sub> ) was determined through the extrapolation of the increased anodic current density to the passive current density.

In addition, in the present work, no pits were observed on the surfaces at the chloride concentrations less than 0.01 kmol/m<sup>3</sup> after measurement of anodic polarization curves. Therefore, it was found that no pitting corrosion took place at the chloride concentration less than 0.01 kmol/m<sup>3</sup>. At a chloride concentration higher than 0.01 kmol/m<sup>3</sup>, 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. 1, and an apparent pitting potential in the same manner was also obtained at the chloride concentrations less than 0.01 kmol/m<sup>3</sup> with no occurrence of pitting corrosion (no pits).

Fig. 3 shows the representative of the anodic polarization curves for type of C276 alloy as a reference in sodium chloride solutions with various chloride concentrations at 293 K. The similar manner was also conducted to obtain the pitting potentials of C 276 at

various chloride concentration as well as those of Ni<sub>3</sub>(Si,Ti). Furthermore, no pits were observed on the surfaces at the chloride concentrations less than 0.05 kmol/m<sup>3</sup> after measurement of anodic polarization curves. In addition, in present work, it was found that no pitting corrosion took place at the chloride concentration less than 0.05 kmol/m<sup>3</sup> at 293 K. At a chloride concentration higher than 0.05 kmol/m<sup>3</sup>, the pitting potential was obtained as shown in the figure inserted in Fig. 3, and an apparent pitting potential in the same manner was also obtained at the chloride concentrations less than 0.05 kmol/m<sup>3</sup> with no occurrence of pitting corrosion.

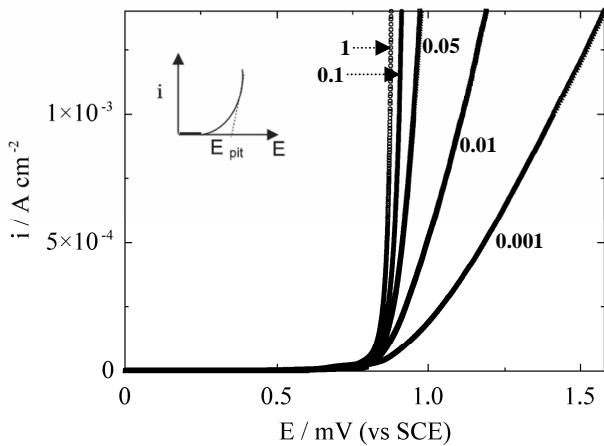


Fig 3. Anodic polarization curves for C 276 alloy with various chloride concentrations (kmol/m<sup>3</sup>) at 293 K.

**B. Effect of chloride concentration**

Fig. 4 shows the relationship between pitting potential ( $E_{pit}$ ) and a logarithm of chloride concentrations for Ni<sub>3</sub>(Si,Ti) and C 276 alloy at 293 K. It was found that pitting potentials of both compounds increased linearly with decreasing chloride concentration up to a certain chloride concentration, below which no pitting corrosion took place as well as S. Wagle and co- worker’s results (Wagle et al., 2011a ; Wagle et al., 2011b). 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 factors of film breakdown rate and repassivation rate are important as well as the pitting corrosion of the as homogenized Ni<sub>3</sub>(Si,Ti)(Wagle et al., 2011a). Below the critical chloride concentration, the repassivation rate is superior to the film breakdown to show no pitting corrosion.

From Fig. 4, it was found that pitting potential of Ni<sub>3</sub>(Si,Ti) was clearly lower than that of C276 alloy at various chloride concentrations up to critical chloride concentrations. This means that Ni<sub>3</sub>(Si,Ti) has worse pitting corrosion resistance than C276 in sodium chloride solutions at 293 K. 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 this table, it was found that the specific pitting potential of Ni<sub>3</sub>(Si,Ti) after

thermomechanical process was found to be lower than that of C276 alloy.

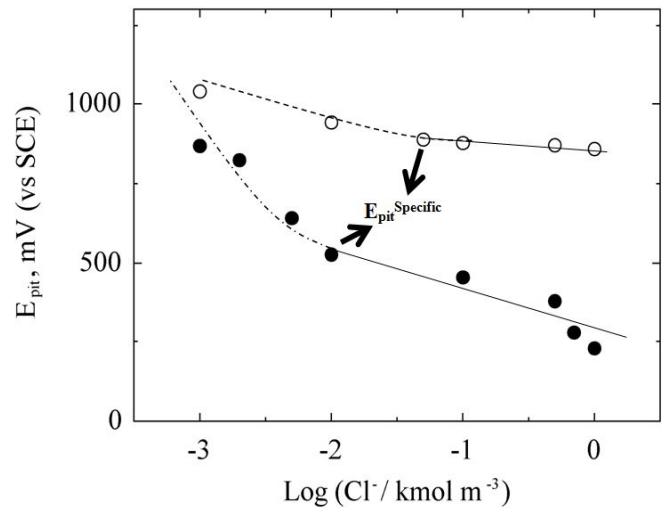


Fig.4 Chloride concentration dependence of pitting potential for ● Ni<sub>3</sub>(Si,Ti) and ○ C276 alloy in sodium chloride solutions at 293 K

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

Compounds	$E_{pit}^{Specific}$ , mV (vs SCE)	$Cl_{cri}$ (kmol/m <sup>3</sup> )
Ni <sub>3</sub> (Si,Ti)	530	0.01
C276	889	0.05

On the other hand, the specific pitting potential of as homogenized Ni<sub>3</sub>(Si,Ti)(Wagle et al.,2011a) was also found to be lower than that of C276 alloy, while specific pitting potential of as homogenized Ni<sub>3</sub>(Si,Ti) (545 mV vs SCE)(Wagle et al.,2011a) was almost the same as that of Ni<sub>3</sub>(Si,Ti) after thermomechanical process (530 mV vs SCE) in the same critical chloride concentration. However, the specific pitting potential of both Ni<sub>3</sub>(Si,Ti) compounds were lower than that of C276 alloy.

**IV. CONCLUSION**

The pitting corrosion behavior of Ni<sub>3</sub>(Si,Ti) intermetallic compound after thermomechanical process was investigated as function of chloride concentration in sodium chloride solutions at 293 K. The results obtained were summarized as follows.

1. The pitting potential decreased with increasing chloride concentration above the critical chloride concentration, below which no pitting corrosion took place.
2. The specific pitting potential of C276 alloy was higher than that of Ni<sub>3</sub>(Si,Ti) compound.
3. The pitting potential of Ni<sub>3</sub>(Si,Ti) compound was lower than that of type of C276 alloy.
4. The pitting corrosion resistance of Ni<sub>3</sub>(Si,Ti) compound was lower than that of type C276 alloy.

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