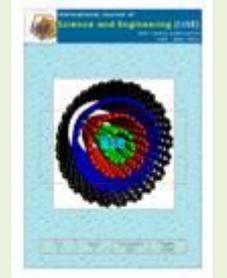




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# Corrosion Behavior of $\text{Ni}_3(\text{Si,Ti}) + 2\text{Mo}$ in Hydrochloric Acid Solution

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**Abstract** - The corrosion behavior of  $\text{Ni}_3(\text{Si,Ti}) + 2\text{Mo}$  intermetallic compound ( $\text{L}_{12}$  and ( $\text{L}_{12} + \text{Ni}_{\text{ss}}$ ) mixture region) has been investigated using an immersion test, polarization method and surface analytical method (scanning electron microscope and energy-dispersive X-Ray spectrometry) in  $0.5 \text{ kmol/m}^3$  hydrochloric acid (HCl) solution at 303 K. In addition, the results obtained were compared to those of the  $\text{L}_{12}$  single-phase  $\text{Ni}_3(\text{Si,Ti})$  intermetallic compound and C 276 alloy. It was found that  $\text{Ni}_3(\text{Si,Ti}) + 2\text{Mo}$  had the preferential dissolution of  $\text{L}_{12}$  with a lower Mo concentration compared to ( $\text{L}_{12} + \text{Ni}_{\text{ss}}$ ) mixture region. From the immersion test and polarization curves,  $\text{Ni}_3(\text{Si,Ti}) + 2\text{Mo}$  and C276 showed the lowest corrosion resistance and the highest corrosion resistance in the solution, respectively. From this work, It implied that unlike C276,  $\text{Ni}_3(\text{Si,Ti}) + 2\text{Mo}$  intermetallic compound was difficult to form a stable passive film in HCl solution as well as  $\text{Ni}_3(\text{Si,Ti})$  in the same solution.

**Keywords** - Intermetallic Compound; Immersion Test; Polarization; Preferential Dissolution

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### I. INTRODUCTION

$\text{Ni}_3(\text{Si,Ti})$  intermetallic compound with an  $\text{L}_{12}$  single-phase structure has particular 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). Furthermore, its strength level was high compared to those of other  $\text{L}_{12}$  ordered intermetallic compounds developed as advanced materials (Kaneno et al.,2008). On the other hand,  $\text{Ni}_3(\text{Si,Ti})$  intermetallic compound has remarkable mechanical properties compared to those of conventional alloys such as nickel-base alloys, mild steels and austenitic stainless steels. In addition, this intermetallic compound has shown an excellent oxidation resistance in air at ambient and elevated temperatures (Kaneno et al.,2007). On the other hand, an improvement in the mechanical property of the  $\text{Ni}_3(\text{Si,Ti})$  compound was attempted with macro-alloying by adding molybdenum, which enhanced tensile strength and hardness, and also improved the elongation at various operational temperatures (Kaneno et al.,2011). In addition,  $\text{Ni}_3(\text{Si,Ti})$  with Mo addition were composed of two regions of the  $\text{L}_{12}$  single-phase and a two phase mixture of  $\text{L}_{12}$  and  $\text{Ni}_{\text{ss}}$ , where  $\text{Ni}_{\text{ss}}$  was a fcc Ni solid solution (Kaneno et al., 2011).

However,  $\text{Ni}_3(\text{Si,Ti})$  intermetallic compound has shown the susceptibility to environmental embrittlement at ambient temperature in moist air and hydrogen gas (Takasugi et al.,1993a,b ; Takasugi et al.,1995). The addition of boron to this compound was conducted to suppress the environmental embrittlement (Takasugi et al.,1995), but led to the intergranular attack for this as-homogenized  $\text{Ni}_3(\text{Si,Ti})$  compound in acidic solutions, due to boron segregation at grain boundaries (Priyotomo et al.,2011) as well as  $\text{Ni}_3(\text{Si,Ti})$  after the thermomechanical process (Priyotomo et al., 2013).

On the other hand, the other researchers found that the homogenized  $\text{Ni}_3(\text{Si,Ti}) + 2\text{Mo}$  intermetallic compound had the lower corrosion resistance than a homogenized  $\text{Ni}_3(\text{Si,Ti})$  intermetallic compound due to preferential dissolution of the  $\text{L}_{12}$  single-phase with lower Mo concentration in comparison with the ( $\text{L}_{12} + \text{Ni}_{\text{ss}}$ ) two phase region in HCl solutions at 303 K (Priyotomo et al.,2011 ; Priyotomo et al.,2012). With regard to the compounds, there is little study on the corrosion behavior of  $\text{Ni}_3(\text{Si,Ti}) + 2\text{Mo}$  after thermomechanical process in HCl solution at 303K. Therefore, the objective of this work is to elucidate the corrosion behavior of  $\text{Ni}_3(\text{Si,Ti}) + 2\text{Mo}$  in HCl solution in comparison with that of the  $\text{Ni}_3(\text{Si,Ti})$  intermetallic

compound after thermomechanical process and C276 alloy.

## II. EXPERIMENTAL

### A. The specimens

Ni-11 at.% Si-7.5 at.% Ti-2 at.% Mo 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. 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 carried out a 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 at 1273K for 1 h. Ni<sub>3</sub>(Si,Ti) intermetallic compound and type of C276 alloy also was as the references for the experiments (Priyotomo et al.,2013). The chemical and nominal compositions of materials are given in Table 1.

### B. Pretreatment of the specimens and test solutions

The specimens were cut into 1.2 mm x 9 mm x 15 mm. Then they were polished to with emery paper to 1000 grit, degreased by using acetone in an ultrasonic cleaner and washed with distilled water. The test solution, 0.5 kmol/m<sup>3</sup> HCl solution, was made by using reagent grade chemicals and distilled water. For microstructure observation before the experiments, galvanostatic etching of the mechanically polished specimens was conducted in a solution that consist of 15 ml of 17.8 kmol/m<sup>3</sup> H<sub>2</sub>SO<sub>4</sub> solution and 85 ml of methanol solution at a current density of 0.446 A/cm<sup>2</sup> for 30 sec at 243K. The aim of galvanostatic etching is to reveal the presence of the phases.

### C. Corrosion test

1) Immersion test and the observation of corroded surface morphology: The immersion test of the mechanically polished specimen was conducted to get a weight loss ( $\Delta W$ ), the difference in weights of the specimens before and after the immersion test, at various immersion times up to a maximum time of 96 hours in HCl solution at 303 K under an open circuit condition. After the experiments, the morphology of the specimen surfaces was investigated by using scanning electron microscope (SEM) and energy-dispersive X-Ray spectrometry.

2) Polarization test: The potential method was used to measure polarization curves of the specimens in HCl solution that contacted with open air at 303 K. The reference and counter electrodes used were Ag/AgCl saturated with KCl and a platinum sheet, respectively. Polarization measurements were conducted in a potential range from -800 mV to 1000 mV vs. Ag/AgCl, where the potential was increased (anodic) or decreased (cathodic) from a corrosion potential with a potential interval of 100 mV (partly 50 mV) and was held for 10 minutes at each potential.

Table 1: Composition and nominal of the materials investigated

Elements	Ni <sub>3</sub> (Si,Ti)+2Mo	Ni <sub>3</sub> (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	2.0	-	17
V	-	-	0.35
Fe	-	-	7
Ti	7.5	9.5	-
W	-	-	4.5
Co	-	-	2.5
<b>ppm</b>			
B	50	-	-

## III. THE RESULTS AND DISCUSSION

### A. Microstructure before corrosion test

Ni<sub>3</sub>(Si,Ti) + 2Mo are composed of L1<sub>2</sub> phase (dark area) and (L1<sub>2</sub> + Ni<sub>ss</sub>) mixture region (white area) as shown in Fig 1. The microstructure of Ni<sub>3</sub>(Si,Ti)+2Mo with dual phases ( L1<sub>2</sub> and mixture region) that were observed, had small and equiaxial grains in L1<sub>2</sub> phase. Furthermore, Kaneno and co-workers have already investigated the microstructure of this compound in detail [5].

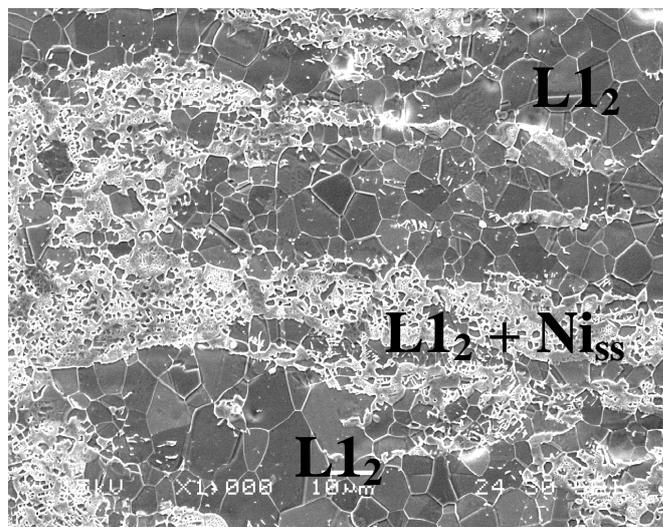


Fig. 1 Microstructure of Ni<sub>3</sub>(Si,Ti)+2Mo before corrosion test

### B. Weight Loss and polarization test

Fig. 2 shows the immersion time dependence of the weight losses for Ni<sub>3</sub>(Si,Ti) +2Mo, Ni<sub>3</sub>(Si,Ti) (Priyotomo et al., 2013) and C 276 (Priyotomo, et al.,2013) in 0.5 kmol/m<sup>3</sup> HCl solution at a temperature of 303 K. The weight losses for these materials tended to increase with immersion time. In addition, from the weight loss, it was found that the corrosion resistance was decreased in the order of C276 > Ni<sub>3</sub>(Si,Ti) > Ni<sub>3</sub>(Si,Ti) +2Mo in the HCl solution.

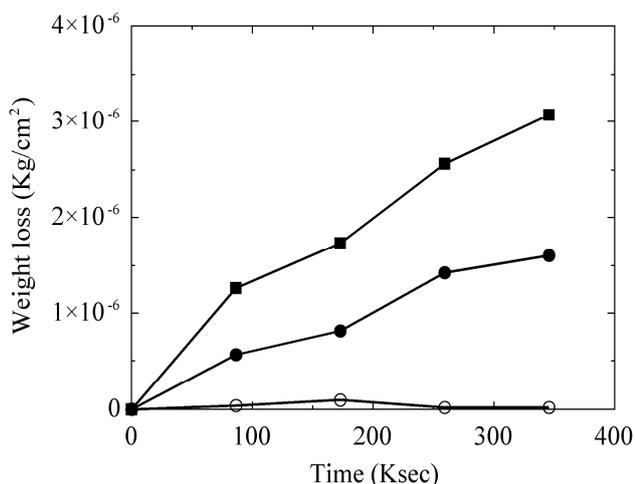


Fig. 2 The weight losses of ● Ni<sub>3</sub>(Si,Ti), ○ C 276, and ■ Ni<sub>3</sub>(Si,Ti)+2Mo as a function of immersion time in 0.5 kmol/m<sup>3</sup> HCl solution at 303 K.

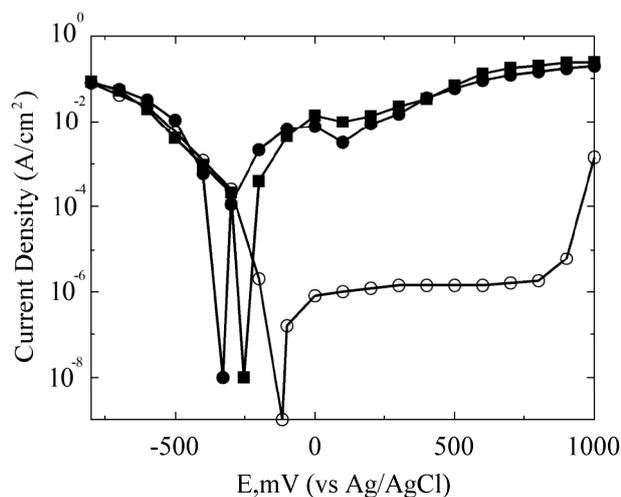


Fig. 3. Polarization curves of ● Ni<sub>3</sub>(Si,Ti), ○ C 276, and ■ Ni<sub>3</sub>(Si,Ti)+2Mo in 0.5 kmol/m<sup>3</sup> HCl solution at 303 K.

The polarization curves of Ni<sub>3</sub>(Si,Ti), Ni<sub>3</sub>(Si,Ti)+2Mo (Priyotomo et al.,2013) and C276 (Priyotomo et al.,2013) in 0.5 kmol/m<sup>3</sup> HCl solution at 303K were shown in Fig. 3, where the polarization curve consists of anodic and cathodic curves. . The anodic polarization curve of Ni<sub>3</sub>(Si,Ti) + 2Mo showed that the anodic current density tended to increase monotonously with increasing potential, which means that the polarization curve did not have the passive region. On the other hand, the anodic polarization curve of Ni<sub>3</sub>(Si,Ti) appeared to have the small active and passive regions. Furthermore, the anodic polarization curve of C276 has the passive region with a wide potential range up to oxygen evolution potential, where this alloy has no active region. The magnitude of anodic current densities of C276 has the lowest than those of Ni<sub>3</sub>(Si,Ti) and Ni<sub>3</sub>(Si,Ti)+2Mo over the whole anodic potential range. In addition, the cathodic current density showed little difference among three materials over the whole cathodic potential range.

From the results obtained in Fig 2 and Fig 3, the following things were summarized.

- (1) The corrosion resistance of C276 was the highest in HCl solution.
- (2) Ni<sub>3</sub>(Si,Ti) showed the higher corrosion resistance than that Ni<sub>3</sub>(Si,Ti)+2Mo solution.
- (3) The results of the immersion test on all materials had a good correspondence with those of the polarization test.

#### C. Corroded surface morphology and elements distribution of corroded compound

Fig. 4a shows the surface morphology of Ni<sub>3</sub>(Si,Ti) + 2Mo after the immersion times of 96 hours in the HCl solution. For Ni<sub>3</sub>(Si,Ti) + 2Mo compound, L<sub>12</sub> phase dissolved preferentially compared to (L<sub>12</sub> + Ni<sub>ss</sub>) mixture region that is, the preferential dissolution of L<sub>12</sub> phase. Furthermore, in the preceding results, the intergranular attack was observed for Ni<sub>3</sub>(Si,Ti) compound in HCl solution (Priyotomo et al., 2011 ; Priyotomo et al., 2013).

On the other hand, from Figs. 4(b-e), Ni observed to be uniformly distributed, whereas Mo was enriched in (L<sub>12</sub> + Ni<sub>ss</sub>) mixture region compared to that in L<sub>12</sub> phase. On the other hand, Si and Ti were enriched in L<sub>12</sub> phase compared to those in (L<sub>12</sub> +Ni<sub>ss</sub>) mixture region. In addition, the surface morphology of Ni<sub>3</sub>(Si,Ti) after the immersion time of 96 h in HCl solution already investigated , where all elements uniformly distributed (Priyotomo et al.,2011 ; Priyotomo et al.,2013).

#### D. The preferential dissolution of L<sub>12</sub> phase in Ni<sub>3</sub>(Si,Ti) + 2Mo

From the results obtained in Section B, the immersion test showed that Ni<sub>3</sub>(Si,Ti)+2Mo intermetallic compound had the preferential dissolution of L<sub>12</sub> phase, but not the intergranular attack such as that of Ni<sub>3</sub>(Si,Ti)(Priyotomo et al.,2011 ; Priyotomo et al.,2013). Furthermore, Ni<sub>3</sub>(Si,Ti) with the single phase of L<sub>12</sub> structure (Priyotomo et al.,2013) has more corrosion resistance than that of Ni<sub>3</sub>(Si,Ti) + 2Mo with L<sub>12</sub> and (L<sub>12</sub> + Ni<sub>ss</sub>) mixture region. This implies that L<sub>12</sub> itself phase has a different corrosion behavior between at single phase and that in (L<sub>12</sub> phase and the mixture region), where the former L<sub>12</sub> phase (single phase) has apparently a lower corrosion rate than the latter (L<sub>12</sub> phase and (L<sub>12</sub>+Ni<sub>ss</sub>)). On the other hand, from the results obtained in Section III.B, the existence of (L<sub>12</sub>+Ni<sub>ss</sub>) mixture region in Ni<sub>3</sub>(Si,Ti)+2Mo compound would lead to the increase in the anodic current density and weight loss in the solution, comparing with Ni<sub>3</sub>(Si,Ti)(Priyotomo et al.,2011).

It is well known that in the case of C276, the addition of Mo with the higher concentration had the excellent corrosion resistance and a stable passive film in chloride solution (Priyotomo et al., 2013). Therefore, on Ni<sub>3</sub>(Si,Ti)+2Mo intermetallic compound, we consider the preferential dissolution of L<sub>12</sub> phase from an amount of Mo in the phase. The amount of Mo was found to be more enriched in (L<sub>12</sub> + Ni<sub>ss</sub>) than in L<sub>12</sub> phase. The (L<sub>12</sub> + Ni<sub>ss</sub>) mixture region would form more stable film than that of L<sub>12</sub> phase (Priyotomo et al., 2012), which means that the former film has a smaller dissolution rate than that of the latter film. This is considered being the causes of the preferential dissolution of L<sub>12</sub> phase.

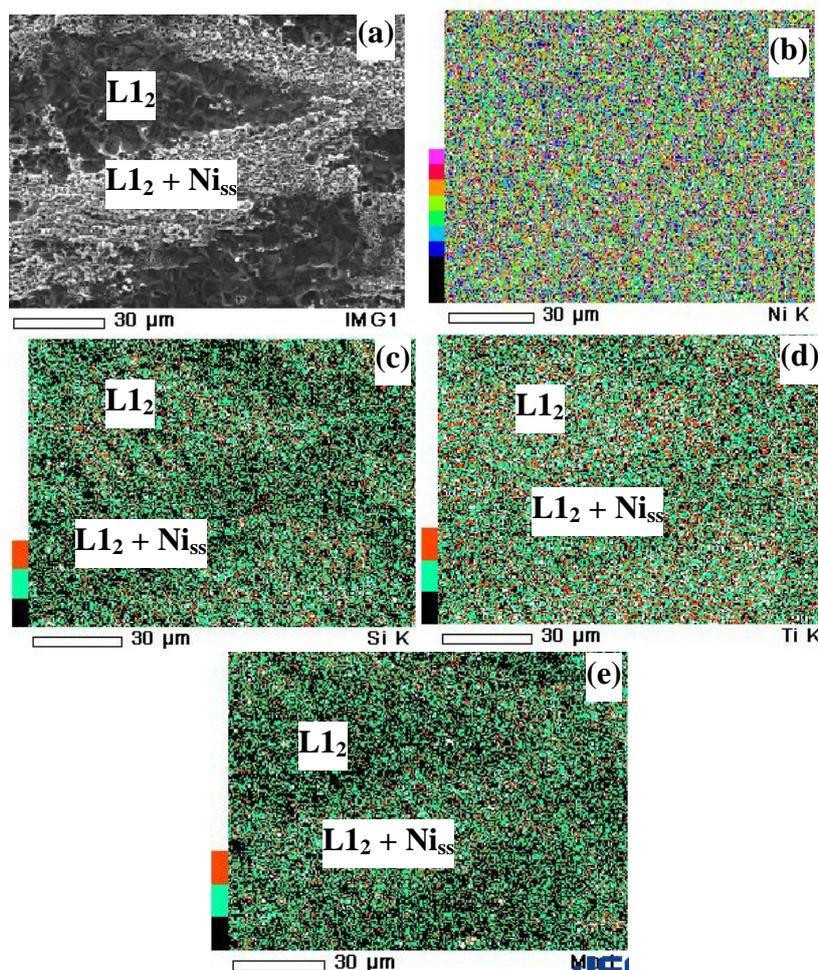


Fig.4 Surface morphology and element distribution of  $\text{Ni}_3(\text{Si,Ti}) + 2\text{Mo}$  after the immersion time of 96 h in  $0.5 \text{ kmol/m}^3$  HCl solution at 303 K, (a) SEM; (b) Ni; (c) Si; (d) Ti; (e) Mo

#### IV. CONCLUSION

The corrosion behavior of  $\text{Ni}_3(\text{Si,Ti}) + 2\text{Mo}$  compound after thermomechanical process in  $0.5 \text{ kmol/m}^3$  HCl solution has been studied and compared with that of  $\text{Ni}_3(\text{Si,Ti})$  compound and C276 alloy. The following things were obtained.

- (1)  $\text{Ni}_3(\text{Si,Ti}) + 2\text{Mo}$  had the preferential dissolution of  $\text{L1}_2$  phase with a lower Mo concentration compared to  $(\text{L1}_2 + \text{Ni}_{\text{ss}})$  mixture region.
- (2) The corrosion resistance of C276 and  $\text{Ni}_3(\text{Si,Ti}) + 2\text{Mo}$  had the highest and the lowest in HCl solution, respectively.
- (3)  $\text{Ni}_3(\text{Si,Ti}) + 2\text{Mo}$  intermetallic compound was difficult to form a stable passive film on the whole surface in the HCl solution as well as  $\text{Ni}_3(\text{Si,Ti})$  compound.

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