Corrosion Behavior of Ni₃(Si,Ti) + 2Mo in Hydrochloric Acid Solution

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Abstract - The corrosion behavior of Ni₃(Si,Ti) + 2Mo intermetallic compound (L1₂ and (L1₂ + Ni₃) 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 kmol/m³ hydrochloric acid (HCl) solution at 303 K. In addition, the results obtained were compared to those of the L1₂ single-phase Ni₃(Si,Ti) intermetallic compound and C276 alloy. It was found that Ni₃(Si,Ti) + 2Mo had the preferential dissolution of L1₂ with a lower Mo concentration compared to (L1₂ + Ni₃) mixture region. From the immersion test and polarization curves, Ni₃(Si,Ti) + 2Mo and C276 showed the lowest corrosion resistance and the highest corrosion resistance in the solution, respectively. From this work, it implied that unlike C276, Ni₃(Si,Ti) + 2Mo intermetallic compound was difficult to form a stable passive film in HCl solution as well as Ni₃(Si,Ti) in the same solution.

Keywords - Intermetallic Compound, Immersion Test, Polarization, Preferential Dissolution

I. INTRODUCTION

Ni₃(Si,Ti) intermetallic compound with an L1₂ 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 L1₂ ordered intermetallic compounds developed as advanced materials (Kaneno et al., 2008). On the other hand, Ni₃(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 Ni₃(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, Ni₃(Si,Ti) with Mo addition were composed of two regions of the L1₂ single-phase and a two phase mixture of L1₂ and Ni₃, where Ni₃ was a fcc Ni solid solution (Kaneno et al., 2011).

However, Ni₃(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 Ni₃(Si,Ti) compound in acidic solutions, due to boron segregation at grain boundaries (Priyotomo et al., 2011) as well as Ni₃(Si,Ti) after the thermomechanical process (Priyotomo et al., 2013).

On the other hand, the other researchers found that the homogenized Ni₃(Si,Ti) + 2Mo intermetallic compound had the lower corrosion resistance than a homogenized Ni₃(Si,Ti) intermetallic compound due to preferential dissolution of the L1₂ single-phase with lower Mo concentration in comparison with the (L1₂ + Ni₃) 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 Ni₃(Si,Ti) + 2Mo after thermomechanical process in HCl solution at 303K. Therefore, the objective of this work is to elucidate the corrosion behavior of Ni₃(Si,Ti) +2Mo in HCl solution in comparison with that of the Ni₃(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. Ni₃(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/m³ 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/m³ H₂SO₄ solution and 85 ml of methanol solution at a current density of 0.446 A/cm² 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 (ΔW), the difference in weights of the specimen 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.

III. THE RESULTS AND DISCUSSION

A. Microstructure before corrosion test
Ni₃(Si,Ti) + 2Mo are composed of L1₂ phase (dark area) and (L1₂ + Ni₃) mixture region (white area) as shown in Fig 1. The microstructure of Ni₃(Si,Ti)+2Mo with dual phases ( L1₂ and mixture region) that were observed, had small and equiaxial grains in L1₂ phase. Furthermore, Kaneno and co-workers have already investigated the microstructure of this compound in detail [5].

B. Weight Loss and polarization test
Fig. 2 shows the immersion time dependence of the weight losses for Ni₃(Si,Ti) + 2Mo, Ni₃(Si,Ti) (Priyotomo et al., 2013) and C 276 (Priyotomo, et al.,2013) in 0.5 kmol/m³ 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 > Ni₃(Si,Ti) > Ni₃(Si,Ti) +2Mo in the HCl solution.
The polarization curves of Ni₃(Si,Ti), Ni₃(Si,Ti)+2Mo (Priyotomo et al., 2013) and C276 (Priyotomo et al., 2013) in 0.5 kmol/m³ HCl solution at 303K were shown in Fig. 3, where the polarization curve consists of anodic and cathodic curves. The anodic polarization curve of Ni₃(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 Ni₃(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 Ni₃(Si,Ti) and Ni₃(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) Ni₃(Si,Ti) showed the higher corrosion resistance than that of Ni₃(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 Ni₃(Si,Ti) + 2Mo after the immersion times of 96 hours in the HCl solution. For Ni₃(Si,Ti) + 2Mo compound, L1₂ phase dissolved preferentially compared to (L1₂ + Ni₃) mixture region that is, the preferential dissolution of L1₂ phase. Furthermore, in the preceding results, the intergranular attack was observed for Ni₃(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 (L1₂ + Niss) mixture region compared to that in L1₂ phase. On the other hand, Si and Ti were enriched in L1₂ phase compared to those in (L1₂ + Niss) mixture region. In addition, the surface morphology of Ni₃(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 L1₂ phase in Ni₃(Si,Ti) + 2Mo

From the results obtained in Section B, the immersion test showed that Ni₃(Si,Ti)+2Mo intermetallic compound had the preferential dissolution of L1₂ phase, but not the intergranular attack such as that of Ni₃(Si,Ti) (Priyotomo et al., 2011; Priyotomo et al., 2013). Furthermore, Ni₃(Si,Ti) with the single phase of L1₂ structure (Priyotomo et al., 2013) has more corrosion resistance than that of Ni₃(Si,Ti) + 2Mo with L1₂ and (L1₂ + Niss) mixture region. This implies that L1₂ itself phase has a different corrosion behavior between at single phase and that in (L1₂ phase and the mixture region), where the former L1₂ phase (single phase) has apparently a lower corrosion rate than the latter (L1₂ phase and (L1₂+Niss)). On the other hand, from the results obtained in Section III.B, the existence of (L1₂+Niss) mixture region in Ni₃(Si,Ti)+2Mo compound would lead to the increase in the anodic current density and weight loss in the solution, comparing with Ni₃(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 Ni₃(Si,Ti)+2Mo intermetallic compound, we consider the preferential dissolution of L1₂ phase from an amount of Mo in the phase. The amount of Mo was found to be more enriched in (L1₂+Niss) than in L1₂ phase. The (L1₂+Niss) mixture region would form more stable film than that of L1₂ 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 L1₂ phase.
IV. CONCLUSION

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

1. Ni$_3$(Si,Ti)+2Mo had the preferential dissolution of L$_1^2$ phase with a lower Mo concentration compared to (L$_1^2$+ Ni$_{ss}$) mixture region.

2. The corrosion resistance of C276 and Ni$_3$(Si,Ti)+2Mo had the highest and the lowest in HCl solution, respectively.

3. Ni$_3$(Si,Ti)+2Mo intermetallic compound was difficult to form a stable passive film on the whole surface in the HCl solution as well as Ni$_3$(Si,Ti) compound.

REFERENCES


