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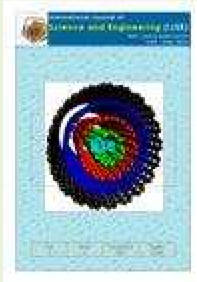

The Effect of Annealing Temperatures after Thermomechanical Process to The Corrosion Behavior of $Ni_3(Si,Ti)$ in Sulfate Solution

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Abstract *- The corrosion behaviour of the intermetallic compounds $Ni_3(Si,Ti)$ ($L1_2$: single phase), has been investigated using an immersion test, polarization method, scanning electron microscope in 0.5 kmol/m^3 H_2SO_4 solution at 303 K. Moreover, the corrosion behaviour of austenitic stainless steel type 304 was studied under the same experimental conditions as reference. It was found that the intergranular attack and uniform attack were observed on $Ni_3(Si,Ti)$ after thermomechanical and annealing processes (1173K and 1273K) respectively in the immersion test. From the immersion test and polarization curves, all annealed $Ni_3(Si,Ti)$ had less corrosion resistance compared to type 304. In addition, $Ni_3(Si,Ti)$ was difficult to form a stable passive film, but not for type 304.*

Keywords *— Intermetallic Compound; Immersion Test; Polarization Curve; Sulfate ion; Corrosion*

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I. INTRODUCTION

An intermetallic compound of $Ni_3(Si,Ti)$ with addition of titanium (Ti) has been considered to be a potential compound which could be applied as high temperature structural materials and chemical parts because this compound shows an increasing strength with increasing operational temperature and also displays remarkable oxidation resistance over a wide range of temperature (Takasugi et al.,1990 ; Takasugi ,2000). Furthermore, this compound has a single phase of $L1_2$ which exhibits a good corrosion resistance (Kaneno et al., 2002). However, Priyotomo and co-workers found the less corrosion resistance of this compound in all acidic solutions where, the types of corrosion are intergranular and uniform (Priyoyotomo et al.,2011 ; Priyotomo et al.,2012). In addition, Wagle (Wagle et al.,2011) and Priyotomo (Priyotomo et al., 2013) also found that the pitting corrosion behavior of the compound with different heat treatment took place in neutral sodium chloride solution. The $Ni_3(Si,Ti)$ intermetallic compounds are susceptible to environmental embritlement (hydrogen embrittlement) at ambient temperature in moist environment (Takasugi et al.,1993a; Takasugi et al.,1993b), where that embrittlement takes place with permeation of atomic hydrogen through electrochemical reaction into the compounds.

Furthermore, the preceding investigation regarding to $Ni_3(Si,Ti)$ carried out the thermomechanical process (TMP) after homogenization process (Takasugi et al., 1990 ; Kaneno et al., 2003). TMP is the combination of deformation process and heat treatment in single system (Poliak et al., 2009). The microstructural control for grain size and texture is possible to be applied by TMP (Kaneno et al.,2003). Priyotomo had already found that the effect of annealing process of Ni3(Si,Ti) after TMP could not enhance their corrosion resistances more effectively in various neutral chloride ion solution (Priyotomo et al.,2013). With regard to $Ni_3(Si,Ti)$ compound, there is little study on the corrosion behavior of $Ni_3(Si,Ti)$ after TMP in aqueous solutions at ambient temperature in sulfate ion (SO_4^{2-}). Therefore, the objective of this work is to elucidate the corrosion behavior of $Ni_3(Si,Ti)$

intermetallic compounds after TMP process in Sulfuric acid (H_2SO_4) solution.

II. EXPERIMENTAL

A. *The specimens*

Ni-11 at.% Si-9.5 at.% Ti compound with the addition of 50 wt. ppm of boron, was prepared by using an high vacuum arc melting furnace under an argon gas atmosphere in chamber of furnace. It was homogenized at 1323K for 2 days under an argon atmosphere and then cooled at a cooling rate of 283K /min in a high vacuum furnace. In TMP process, an ingot was carried out a warm rolling at 573K in a muffle furnace until reaching the certain thickness and then a cold rolling until 1.2 mm of thickness in 75 % reduction. After obtaining a cold-rolled thin sheet, this sheet was finally annealed from 873 K to 1273 K for 1 hour by using a vacuum furnace, where annealing process metal is the heating of metal to a specific temperature and then cooled at a cooling rate of 283K /min. The identification of $Ni_3(Si,Ti)$ intermetallic compound for its chemical composition, had been investigated by an author colleague and the author[6] at Osaka Prefecture University, where the author received that intermetallic compound for this research. Austenitic stainless steel type 304 was as the reference for the research. The chemical composition of prepared materials are given in Table 1.

Table 1 : Composition of the materials investigated

Elements	$Ni_3(Si,Ti)$	Type 304
	At.%	
C	-	0.027
Si	11.0	0.68
Mn	-	0.947
P	-	0.047
S	-	0.006
Ni	79.5	7.6
Cr	-	19.34
Mo	-	-
V	-	-
Fe	-	71.4
Ti	9.5	-
W	-	-
Co	-	-
	ppm	
B	50	-

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 grinded and polished to 1.0 micrometer alumina paste, degreased by acetone in an ultrasonic cleaner and washed with distilled water. The test solution, 0.5 kmol/m^3 sulfuric acid (H_2SO_4) solution, was prepared by reagent grade chemicals and distilled water. For microstructure observation, galvanostatic etching of the mechanically polished specimens was carried out in a solution consisting of 15 ml of 17.8 kmol/m^3 H_2SO_4 and 85 ml of methanol at an applied current density of 0.446 A/cm^2 for 30 seconds at a temperature of 243 K.

C. *Corrosion tests*

1) Immersion test : The immersion test of the polished specimen was carried out to obtain a weight loss (ΔW), 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 0.5 kmol/m^3 H_2SO_4 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).

2) Polarization test : The potential step method was used to measure polarization curves of the specimens in 0.5 kmol/m^3 H_2SO_4 solution open to air at 30^0C. The reference and counter electrodes used were Ag/AgCl saturated with KCl and a platinum sheet, respectively. Polarization measurements were carried out in a potential range from -1073 mV to 1273 mV vs. Ag/AgCl where the potential was increased or decreased from a rest potential with a potential interval of 100 mV (partly 50 mV) and was held for 10 minutes at each potential.

III. RESULTS AND DISCUSSIONS

A. *Microstructures*

Figs 1 (a-e) show the microstructures of $Ni_3(Si,Ti)$ intermetallic compund at various annealed temperatures (873K-1273K) before experiment. The morphology of their surfaces could be revealed by galvanostatic etching method. At the temperature of 873K, the recrystallization process took place which new small grains appear at grain boundaries. In addition, the process of recrystallization of deformed metal is the formation of new nearly defect-free and the growth of these into the surrounding deformed metal (Heller et al.,1984). Furthermore, at the temperature of 873K, the primary recrystallization step took place in nucleating new grains (Bunge et al.,1996). From 973K to 1273K, the new grains grow to became larger with the average grains of 30 μm. At these range of temperature, when the metal is annealed at a higher temperature after the completion of primary recrystallization, specific grains in the primary recrystallized structure consume other grains in the structure and grow into coarse grains (Ushigami et al., 2013). This step is defined secondary recrystallization (Ushigami et al., 2013).

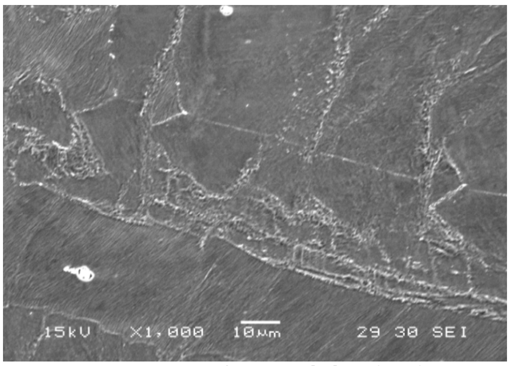

Fig 1a. Microstructure of as annealed $Ni_3(Si,Ti)$ at 873K before experiment

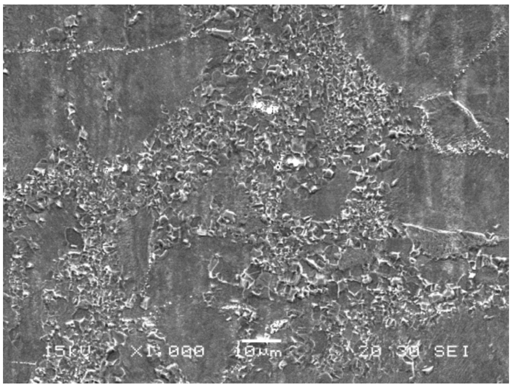

Fig 1b. Microstructure of as annealed $Ni_3(Si,Ti)$ at 973K before experiment

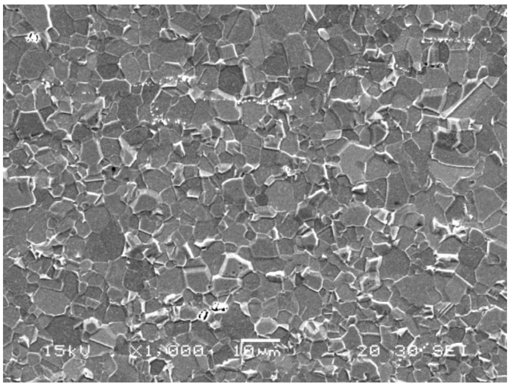

Fig 1c. Microstructure of as annealed $Ni_3(Si,Ti)$ at 1073K before experiment

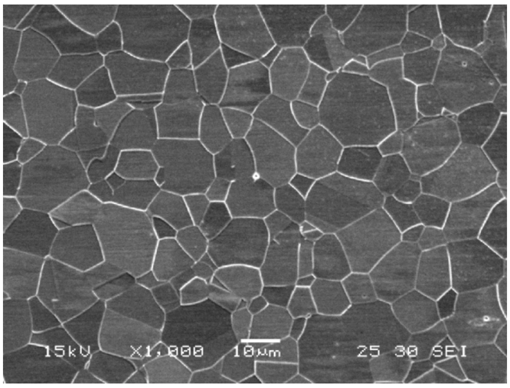

Fig 1d. Microstructure of as annealed $Ni_3(Si,Ti)$ at 1173K before experiment

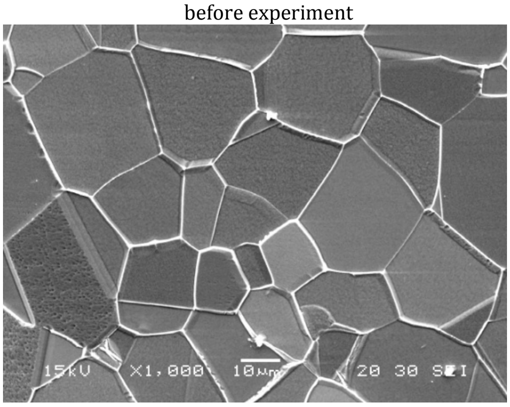

Fig 1e. Microstructure of as annealed $Ni_3(Si,Ti)$ at 1273K before experiment

B. Weight loss, polarization test and surface morphology of corroded compounds

Fig. 2 shows the weight losses of $Ni_3(Si,Ti)$ intermetallic compounds after annealing process at 873K; 973K; 1073K; 1173K and 1273K; and type 304 as a function of immersion time in 0.5 kmol/m^3 H_2SO_4 solution at 303 K. The weight losses for these compounds increase with immersion time. The highest and lowest weight losses were annealed $Ni_3(Si,Ti)$ at 873 K and type 304. The magnitude of weight losses for various annealed $Ni_3(Si,Ti)$ were more than one order higher compared to that of weight loss for type 304. The corrosion resistance was found to order of type 304 > as annealed Ni3(Si,Ti) at 1273K > as annealed Ni3(Si,Ti) at 1173K > as annealed Ni3(Si,Ti) at 973K > as annealed Ni3(Si,Ti) at 1073K > as annealed Ni3(Si,Ti) at 873K.

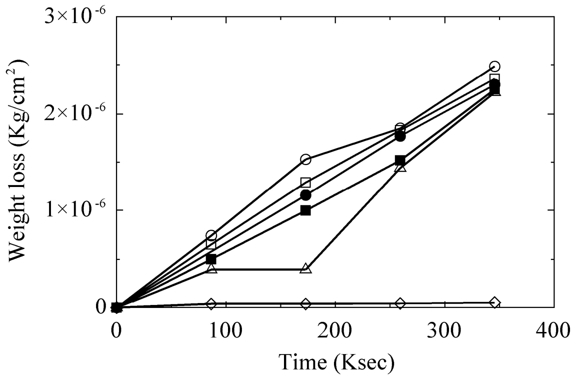

Fig 2. The weight losses of $Ni_3(Si,Ti)$ after annealing process at ○ 873K; ● 973K; □1073K; ■1173K and △1273K; and ◇ type 304 as a function of immersion time in 0.5 kmol/m^3 H_2SO_4 solution at 303 K.

Fig.3 shows the polarization curves of $Ni_3(Si,Ti)$ intermetallic compound after annealing process at 873K; 973K; 1073K; 1173K and 1273; and type 304 in 0.5 kmol/m^3 H_2SO_4 solution at 303K. By comparing the polarization curves in different annealing temperatures, the corrosion potential tend to shift towards positive direction in increasing annealing temperatures. In addition, the corrosion current densities (I_{corr}) of various annealed $Ni_3(Si,Ti)$ decrease with an increase in annealing temperatures. The magnitude of corrosion current densities of various annealed $Ni_3(Si,Ti)$ were more than two or three orders compared to that of type 304.

Furthermore, the anodic polarization curves of various annealed $Ni_3(Si,Ti)$ the increase in anodic current with increasing potential without the passive region up to oxygen evolution potential where those had almost same active region with a low peak current density. On the other hand, type 304 showed an active region with a very low peak current density and a wide passive region up to the oxygen evolution potential. On the basis of the results, it implies that there is no clear passive region on various annealed $Ni_3(Si,Ti)$ compared to type 304.

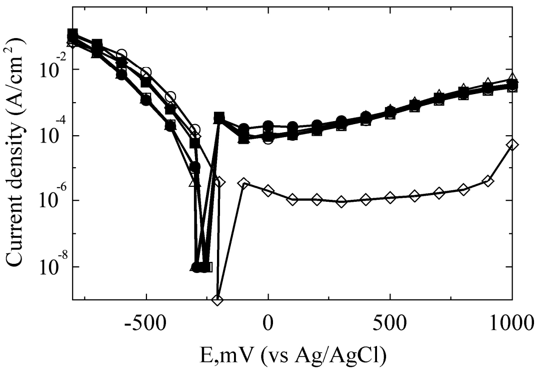

Fig 3. The polarization curves of Ni_3(Si,Ti) after annealing process at ○ 873K; ● 973K; □1073K; ■1173K and △1273; and ◇ type 304 in 0.5 kmol/m³ H_2SO_4 solution at 303K.

Table 2. The results of polarization test for materials in 0.5 kmol/m³ H_2SO_4 solution at 303 K

Materials	E_{corr} (mV vs Ag/AgCl)	I_{corr} (A/cm²)
Annealed Ni_3(Si,Ti) at 873 K	-262	5×10^{-6}
Annealed Ni_3(Si,Ti) at 973 K	-292	5×10^{-7}
Annealed Ni_3(Si,Ti) at 1073 K	-248	6.5×10^{-7}
Annealed Ni_3(Si,Ti) at 1173 K	-258	4.5×10^{-7}
Annealed Ni_3(Si,Ti) at 1273 K	-230	4×10^{-7}
Type 304	-208	4×10^{-9}

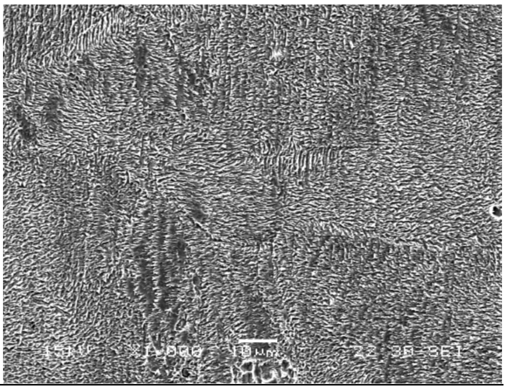

Fig 4a. Microstructure of as annealed Ni_3(Si,Ti) at 873 K after immersion time 96 h in 0.5 kmol/m³ H_2SO_4 solution at 303 K.

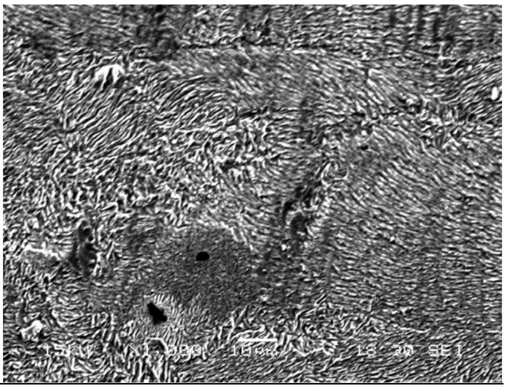

Fig 4b. Microstructure of as annealed Ni_3(Si,Ti) at 973 K after immersion time 96 h in 0.5 kmol/m³ H_2SO_4 solution at 303 K.

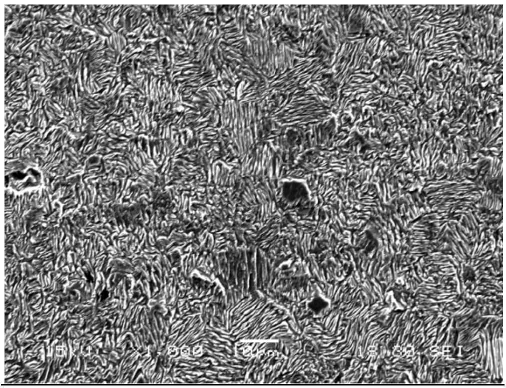

Fig 4c. Microstructure of as annealed Ni_3(Si,Ti) at 1073 K after immersion time 96 h in 0.5 kmol/m³ H_2SO_4 solution at 303 K.

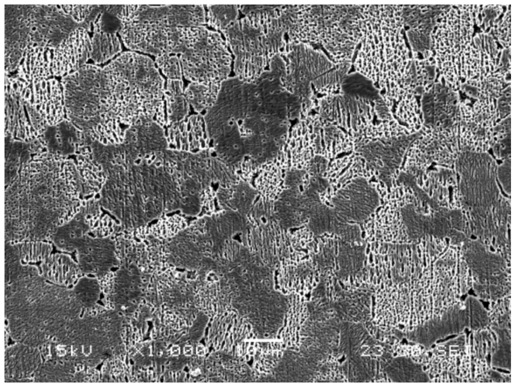

Fig 4d. Microstructure of as annealed Ni_3(Si,Ti) at 1173 K after immersion time 96 h in 0.5 kmol/m³ H_2SO_4 solution at 303 K.

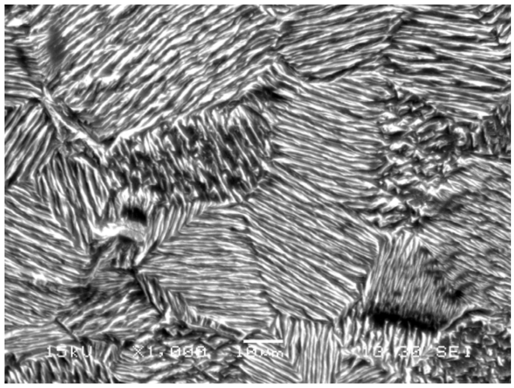

Fig 4e. Microstructure of as annealed Ni_3(Si,Ti) at 1273 K after immersion time 96 h in 0.5 kmol/m³ H_2SO_4 solution at 303 K.

Figs. 4(a-e) show the corroded surface morphology of various annealed Ni_3(Si,Ti) intermetallic compounds after the immersion time of 96 hours in 0.5 kmol/m³ H_2SO_4 solution. On the basis of visual observation on Figs. 4(a-e), it was found that the surface morphology of as annealed Ni_3(Si,Ti) at the temperatures of 873 K, 973 K and 1073 K showed uniform corrosion. On the other hand, intergranular attack in grain boundaries and uniform corrosion in grains took place on the surface of as annealed Ni_3(Si,Ti) at the temperatures of 1173 K and 1273 K.

C. The effect of annealing temperatures to corrosion properties of Ni_3(Si,Ti) in sulfate ion

From the previous sections, with regard to the corrosion tests for as-annealed Ni_3(Si,Ti) at temperatures of 873K, 973K, 1073K, 1173K, 1273K, it was found that the magnitude of weight losses and corrosion current densities of these intermetallic compounds tended to be almost same, but not type 304. Thus, it is elucidated in three following things :

1. After TMP, the effect of annealing process of Ni_3(Si,Ti) intermetallic compounds have no much benefit to increase their corrosion resistances effectively .
2. The corrosion resistance of as-annealed Ni_3(Si,Ti) at 1273K is little higher than that of other as-annealed Ni3(Si,Ti) intermetallic compounds below 1273 K.
3. The highest corrosion susceptibility take places on as-annealed Ni_3(Si,Ti) at 1073 K.

The corrosion susceptibility of as-annealed Ni_3(Si,Ti) at 1073 tends to rise as well as this compound in hydrochloric acid solution (Priyotomo et al.,2013) and Ni_3Al in chloride solution (Oluyemi et al.,2011). The corrosion current density of Ni_3Al intermetallic compound within the temperature range from 973K up to 1073K, could be corresponded to the incomplete progress of the heat-activated processes beginning in places of highest concentration of stresses and, in consequence, creating the local electrochemical micro-cells (Oluyemi et al.,2011). Therefore, this idea can be applied to consider the present result. Moreover, the further investigation will be carried out to elucidate this idea in more detail.

On the previous paper, Priyotomo already had elucidated that the corrosion resistance of Ni_3(Si,Ti) at various annealing temperatures was higher than that of type 304 (Priyotomo et al.,2013) In the H_2SO_4 solution which is very aggressive and strong oxidizing agent, it is known that the austenitic stainless steel such as types 304 has good corrosion resistance compared to as annealed Ni_3(Si,Ti) at various temperatures . Therefore, type 304 was more resistant to sulfate ion attack than as annealed Ni_3(Si,Ti) but not in HCl solution (Priyotomo et al.,2013).

Furthermore, In Fig. 3, the range of a passive region on type 304 is approximately from + 100 mV to + 800 mV where that of all annealed Ni_3(Si,Ti) is only from -100 mV to 0 mV. This means that a stable film of type 304 could be formed easily compared to all annealed Ni_3(Si,Ti). Moreover, the passive film of Ni_3(Si,Ti) was easy to be dissolved out to solution. This implies that the film of Ni_3 (Si,Ti) could not inhibit a direct dissolution from metal surface and influence the corrosion resistance.

IV. CONCLUSIONS

1. The increase of annealing temperature on Ni_3(Si,Ti) intermetallic compounds after thermomechanical process could not enhance their corrosion resistances significantly.
2. The corrosion resistance of Ni_3(Si,Ti) after annealing process at 1273K is little higher than that of the other Ni_3(Si,Ti) intermetallic compounds, while that of as annealed Ni_3(Si,Ti) at 1073K decreases compared to that of this compound at 973K .
3. All Ni_3(Si,Ti) intermetallic compounds had less corrosion resistance compared to type 304.
4. The surface morphology of as annealed Ni_3(Si,Ti) at 873 K, 973 K and 1073 K showed uniform attack. The intergranular attack in grain boundaries and uniform corrosion in grains took place on the surface of as annealed Ni_3(Si,Ti) at the 1173 K and 1273 K.

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