

Research Article

The Corrosion Behavior of Ni₃Al/Ni₃V Two-Phase Intermetallic Compounds in Various Acidic Solutions

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The corrosion behavior of the Ni₃Al/Ni₃V two-phase intermetallic compounds with and without minor elements (Nb, Co, and Cr) to be composed of L₁₂ phase (Ni₃Al) and a mixed phase of L₁₂ (Ni₃Al) and D0₂₂ (Ni₃V) has been investigated by using an immersion test in 0.5 kmol/m³ HCl, H₂SO₄, and HNO₃ solutions. The surface morphology was observed before and after the immersion test by scanning electron microscope (SEM). The results were compared to those of the L₁₂ single-phase Ni₃(Si,Ti) and austenitic stainless steel type 304. In all acidic solutions, preferential dissolution of (L₁₂ + D0₂₂) phase was found in Ni₃Al/Ni₃V, but no intergranular attack, whereas the attacks took place on Ni₃(Si,Ti). The Ni₃Al/Ni₃V showed a higher corrosion resistance in HCl solution and a lower resistance in HNO₃ solution than Ni₃(Si,Ti) and type 304. The addition of the minor elements enhanced corrosion resistance in HNO₃ solution, but not clearly in HCl and H₂SO₄ solutions. In HCl and H₂SO₄, their weight losses during the immersion test were almost the same.

1. Introduction

Recently, Ni-Al-V intermetallic compounds with a two-phase microstructure of Ni₃Al (L₁₂) and Ni₃V (D0₂₂) phases have been developed by Takasugi et al. [1–13] and are confirmed to exhibit a highly coherent interface between these constituent phases. They have superior mechanical properties (i.e., high creep rupture life, high hardness, low thermal expansion, and better thermal conductivity) and also have high tensile strength and fracture toughness over a broad range of temperature in comparison with those of Inconel 750, Inconel 718 and Hastelloy [1–13]. Therefore, the Ni₃Al/Ni₃V two-phase intermetallic compounds are a candidates as materials in land-based, marine-based, and aero-gas turbine industries (turbine blade), high strength nut and bolt, and high temperature bearing or high temperature tool [8, 9, 14]. However, many studies revealed that the intermetallic compounds containing aluminum are very susceptible to hydrogen embrittlement [15–18], where hydrogen embrittlement takes place with permeation of

atomic hydrogen formed by corrosion reaction into the compounds. Hence, to suppress this environmental embrittlement a small amount of boron was added to these compounds. However, it was reported that the boron segregation at grain boundaries became the preferential dissolution site and led to the intergranular attack in the L₁₂ single-phase Ni₃(Si,Ti) [19].

Furthermore, Ni base intermetallic compounds such as single-phase Ni₃(Si,Ti) have attractive properties for high-temperature structural material (e.g., high phase stability and strength at high temperature), but the intermetallic compounds have been shown to suffer from (1) poor ductility at room temperature and low strength at high temperature, and (2) to have the decrease in strength at high temperature. However, multiphase intermetallic compounds such as Ni₃Al/Ni₃V two-phase intermetallic compounds were found to improve these weakness points [13].

At present, with regard to the Ni₃Al/Ni₃V two-phase intermetallic compounds, there are few studies on their

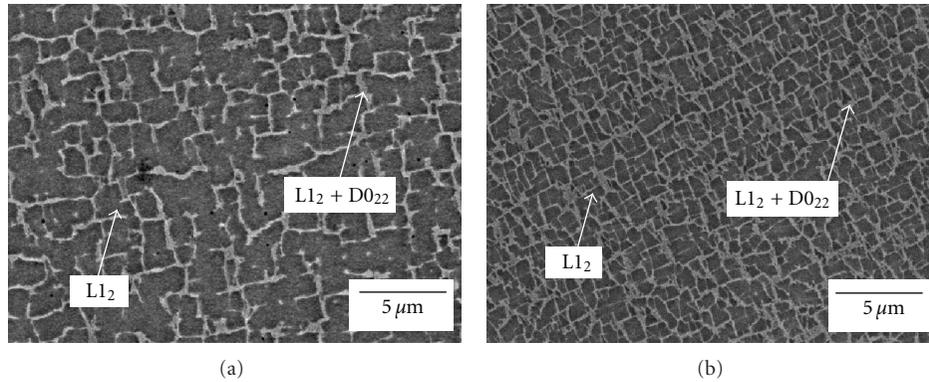


FIGURE 1: Microstructures of $\text{Ni}_3\text{Al}/\text{Ni}_3\text{V}$ two-phase intermetallic compounds: (a) type 1 and (b) type 2 before experiments and after galvanostatic etching.

corrosion behavior in aqueous solutions at ambient temperature. Therefore, the purpose of this work is to elucidate the corrosion behavior of the $\text{Ni}_3\text{Al}/\text{Ni}_3\text{V}$ two-phase intermetallic compounds with and without minor elements of Nb, Co, and Cr in HCl, H_2SO_4 , and HNO_3 solutions and to compare with that of L1_2 single-phase $\text{Ni}_3(\text{Si},\text{Ti})$ intermetallic compound and austenitic stainless steel type 304.

2. Experimental

2.1. The Specimens. The $\text{Ni}_3\text{Al}/\text{Ni}_3\text{V}$ two-phase intermetallic compounds with and without minor elements used in the present study were fabricated from the raw materials of 99.9 wt% Ni, 99.9 wt% Al, 99.9 wt% V, 99.9 wt% Nb, 99.9 wt% Co, and 99.9 wt% Cr. These compounds were prepared as buttons by using an arc melting method under an argon gas atmosphere using a nonconsumable tungsten electrode on a copper hearth. A small amount of boron was added to suppress an intergranular fracture in environments such as air, water, and hydrogen gas [1–13]. Then the button ingot was homogenized at 1553 K for 3 h in vacuum and then furnace cooled. The plate specimens with a 1 mm thickness were prepared by cutting perpendicular to the basal plane of the homogenized button, and then test specimens were cut to the geometry of 1.0 mm \times 10.0 mm \times 20.0 mm by using an electrodischarge machine. The nominal chemical compositions of two types of $\text{Ni}_3\text{Al}/\text{Ni}_3\text{V}$ two-phase intermetallic compounds (hereafter referred to as a type 1 without minor elements and type 2 with minor elements) were shown in Table 1. Here, major alloy elements are Ni, Al, and V and minor elements such as Nb, Co, and Cr are added at the levels of several atomic percents. The addition of Co and Cr was reported to improve oxidation property, while that of Nb to improve high temperature strength and wear properties [8].

2.2. Pretreatment of the Specimens and Test Solutions. The specimens homogenized were cut into 1.2 mm \times 9 mm \times 15 mm. Then they were polished to 1.0 micrometer alumina

paste, degreased by acetone in an ultrasonic cleaner and washed with distilled water. The test solutions, 0.5 kmol/m³ HCl, H_2SO_4 , and HNO_3 , were prepared by reagent grade chemicals and distilled water. For microstructure observation, galvanostatic etching of the mechanically polished specimens was conducted in a solution consisting of 15 mL of 17.8 kmol/m³ H_2SO_4 and 85 mL of methanol at a current density of 0.446 A/cm² for 30 sec at a temperature of 243 K.

2.3. Corrosion Test. The corrosion test of the mechanically polished specimen was conducted by immersion in the three acidic solutions at 303 K under an open circuit condition. A corrosion weight loss (ΔW) was estimated from 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. After the experiments, the morphology of the specimen surfaces was observed by using scanning electron microscope (SEM).

3. Results and Discussion

3.1. Microstructure of $\text{Ni}_3\text{Al}/\text{Ni}_3\text{V}$ Two-Phase Intermetallic Compounds. The $\text{Ni}_3\text{Al}/\text{Ni}_3\text{V}$ two-phase intermetallic compound exhibited the two phases composed of the cuboidal L1_2 precipitate and ($\text{L1}_2 + \text{D0}_{22}$) phase [1, 2] as shown in the magnified photos in Figure 1. Furthermore, Figure 1 shows the microstructure of the $\text{Ni}_3\text{Al}/\text{Ni}_3\text{V}$ two-phase intermetallic compound after the galvanostatic etching. The intermetallic compound consists of two regions of an L1_2 phase of Ni_3Al (dark areas) and a mixed phase of L1_2 of Ni_3Al and D0_{22} of Ni_3V (white areas). In addition, Figure 1 clearly shows that the size of the cuboidal L1_2 precipitate decreases with decreasing the Al content: in other words, a volume fraction of the cuboidal L1_2 precipitate increases with the increase in the Al content in the compounds. The observed microstructures were consistent with those reported in the previous studies [1–13].

3.2. Weight Loss. Figure 2 shows the change in weight loss with immersion time for type 1 and type 2 in 0.5 kmol/m³

TABLE 1: Chemical compositions of the materials investigated.

Alloy	At%														ppm
	C	Si	Mn	P	Nb	S	Ni	Cr	Co	Mo	Al	Fe	V	Ti	
Type 1	—	—	—	—	—	—	75	—	—	—	12	—	13	—	100
Type 2	—	—	—	—	3	—	70.5	3	3	—	10	—	10.5	—	100

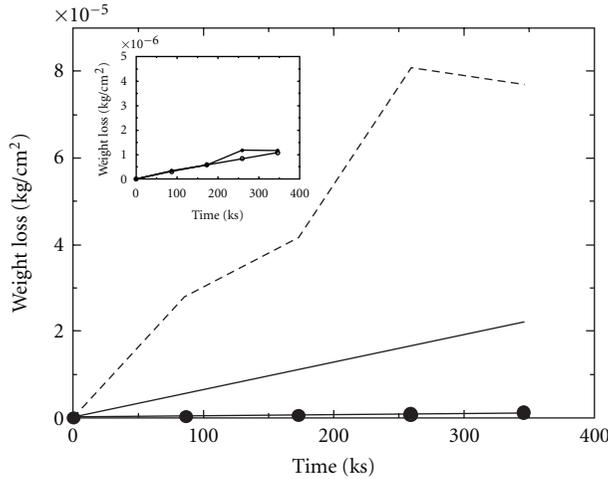


FIGURE 2: The weight losses of $\text{Ni}_3\text{Al}/\text{Ni}_3\text{V}$ two-phase intermetallic compounds: \bullet type 1, \circ type 2, (solid line) $\text{Ni}_3(\text{Si},\text{Ti})$, and (dotted line) Type 304 as a function of immersion time in 0.5 kmol/m^3 HCl solution at 303 K.

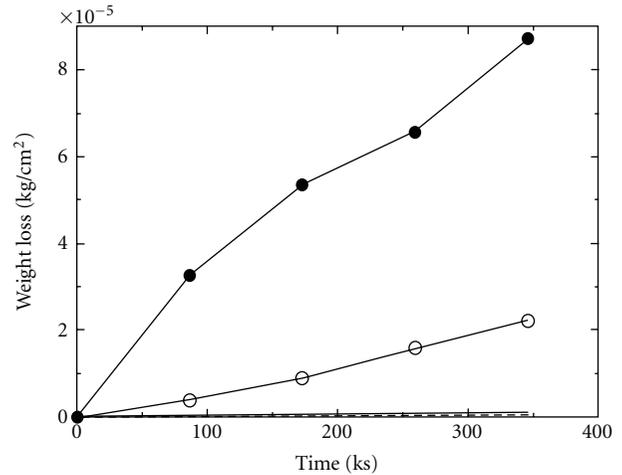


FIGURE 4: The weight losses of $\text{Ni}_3\text{Al}/\text{Ni}_3\text{V}$ two-phase intermetallic compounds: \bullet type 1, \circ type 2, (solid line) $\text{Ni}_3(\text{Si},\text{Ti})$, and (dotted line) Type 304 as a function of immersion time in 0.5 kmol/m^3 HNO_3 solution at 303 K.

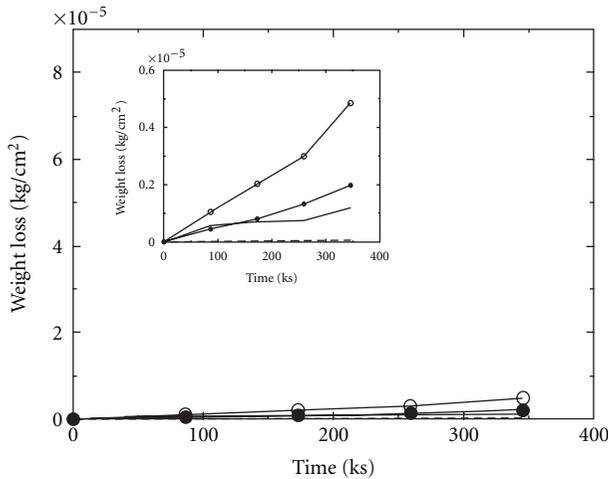


FIGURE 3: The weight losses of $\text{Ni}_3\text{Al}/\text{Ni}_3\text{V}$ two-phase intermetallic compounds: \bullet type 1, \circ type 2, (solid line) $\text{Ni}_3(\text{Si},\text{Ti})$, and (dotted line) Type 304 as a function of immersion time in 0.5 kmol/m^3 H_2SO_4 solution at 303 K.

HCl solution at 303 K, where that for the L1_2 single-phase $\text{Ni}_3(\text{Si},\text{Ti})$ and austenitic stainless steel type 304 was shown for comparison [19]. The weight losses of both compounds were found to be significantly lower than those of $\text{Ni}_3(\text{Si},\text{Ti})$ and type 304. In addition, in the figure magnified in Figure 2,

the weight loss for type 1 was almost the same as that for type 2 over the whole immersion time.

Figure 3 shows the change in weight loss with immersion time for type 1 and type 2 in 0.5 kmol/m^3 H_2SO_4 solution at 303 K, where that for $\text{Ni}_3(\text{Si},\text{Ti})$ and type 304 was also shown for comparison [19]. The weight losses of $\text{Ni}_3(\text{Si},\text{Ti})$ and type 304 were much smaller than those in Figure 2, whereas those of type 1 and type 2 became slightly larger than those in Figure 2. Furthermore, from the figure magnified in Figure 3, it was found that the weight losses of both type 1 and type 2 were larger than those of $\text{Ni}_3(\text{Si},\text{Ti})$ and type 304, and the weight loss of type 2 was larger than that of type 1.

Figure 4 shows the change in weight loss with immersion time for type 1 and type 2 in 0.5 kmol/m^3 HNO_3 solution at 303 K, where that for $\text{Ni}_3(\text{Si},\text{Ti})$ and type 304 was also shown for comparison [19]. In this solution, the weight losses of both type 1 and type 2 were larger than those of $\text{Ni}_3(\text{Si},\text{Ti})$ and type 304. This result was found to be clearly different from that in the HCl solution. In addition, the weight loss of type 1 was larger than that of type 2.

From the results obtained, it was found that the magnitude of weight losses for type 1 and type 2 in acidic solutions increased in order of $\text{HNO}_3 > \text{H}_2\text{SO}_4 > \text{HCl}$, while that for $\text{Ni}_3(\text{Si},\text{Ti})$ and type 304 increased in order of $\text{HCl} > \text{H}_2\text{SO}_4 > \text{HNO}_3$ solutions.

3.3. Surface Morphology of $\text{Ni}_3\text{Al}/\text{Ni}_3\text{V}$ Two-Phase Intermetallic Compounds after Immersion Test. Figure 5 shows the

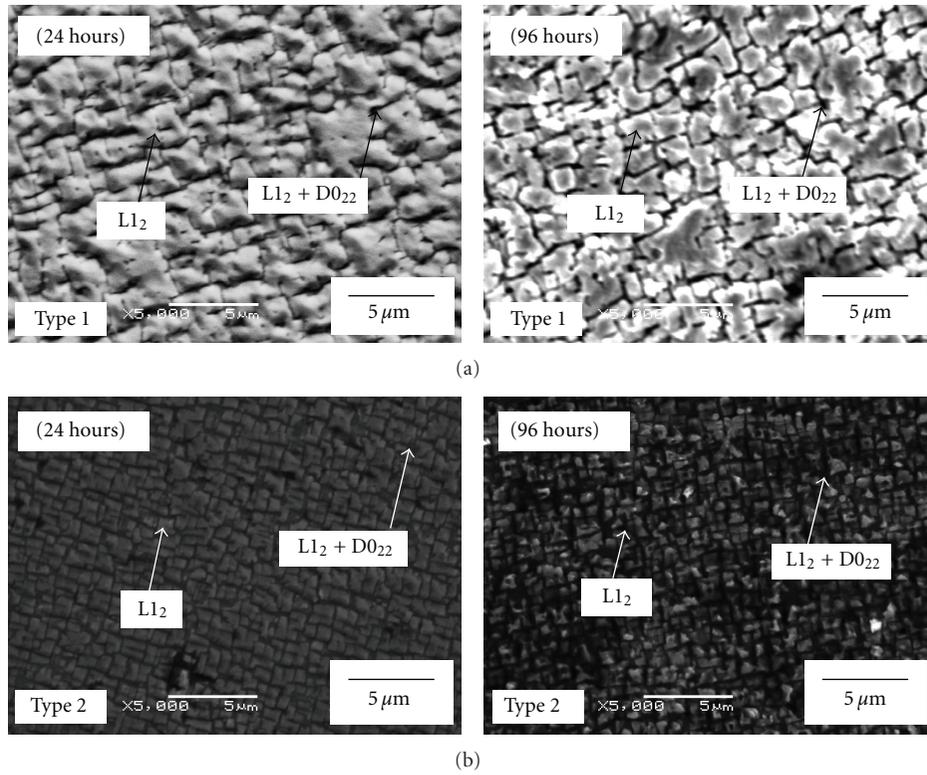


FIGURE 5: SEM microstructures of Ni₃Al/Ni₃V two-phase intermetallic compounds: (a) type 1 and (b) type 2 after the immersion times of 24 hours and 96 hours in 0.5 kmol/m³ HCl solution at 303 K.

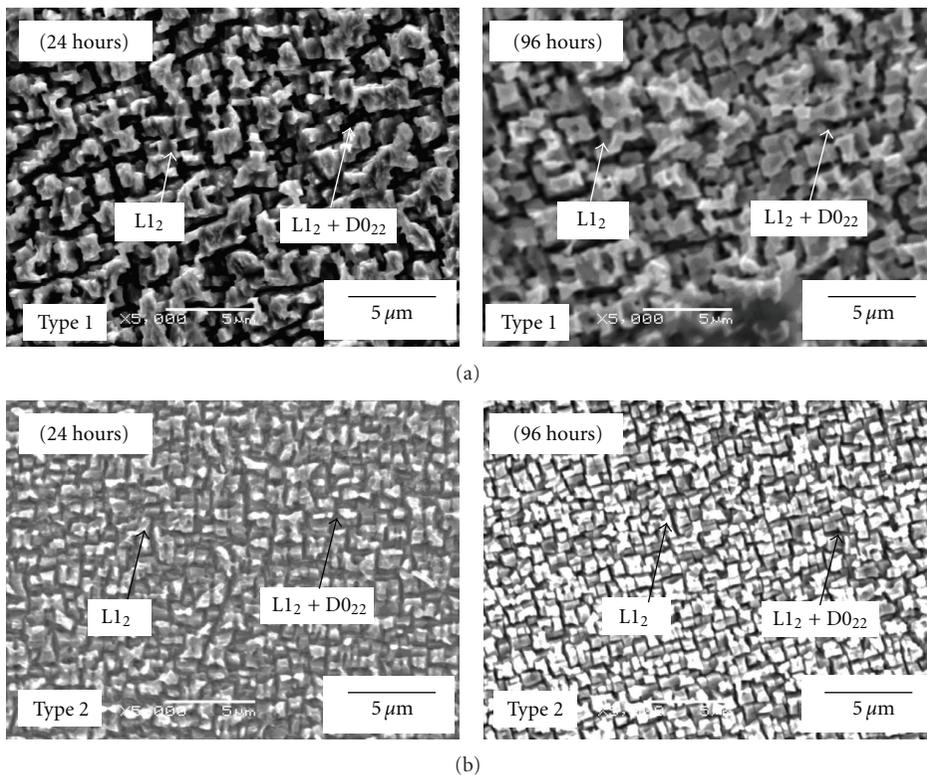


FIGURE 6: SEM microstructures of Ni₃Al/Ni₃V two-phase intermetallic compounds: (a) type 1 and (b) type 2 after the immersion times of 24 hours and 96 hours in 0.5 kmol/m³ H₂SO₄ solution at 303 K.

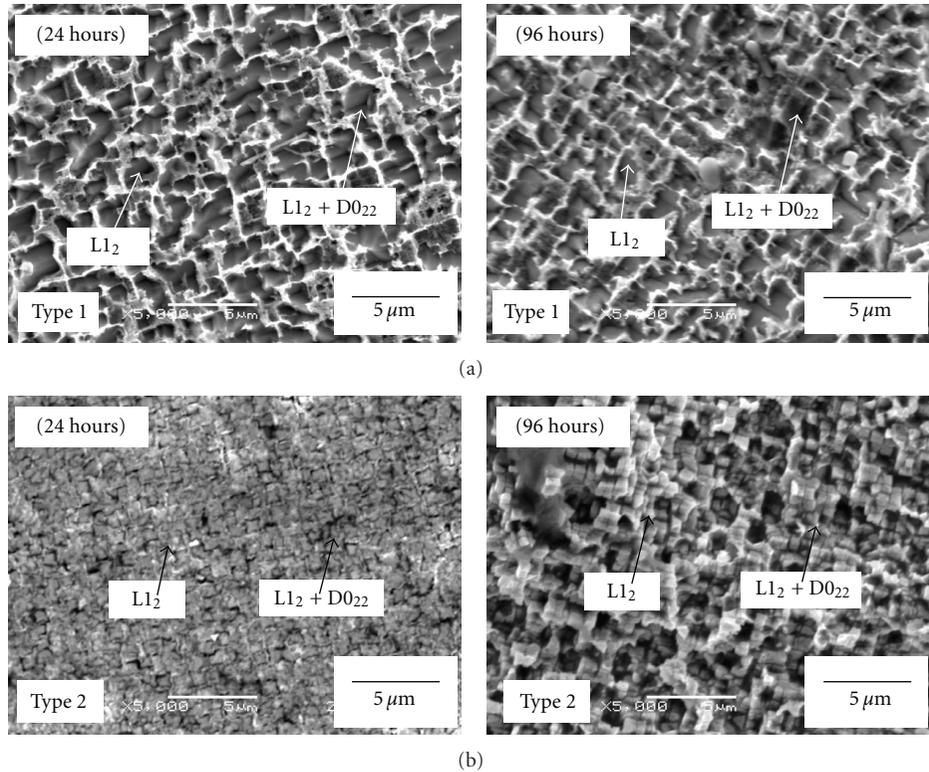


FIGURE 7: SEM microstructures of $\text{Ni}_3\text{Al}/\text{Ni}_3\text{V}$ two-phase intermetallic compounds: (a) type 1 and (b) type 2 after the immersion times of 24 hours and 96 hours in $0.5 \text{ kmol/m}^3 \text{ HNO}_3$ solution at 303 K.

surface morphologies of type 1 and type 2 at the immersion times of 24 hours and 96 hours in the HCl solution. In the HCl solution, a preferential dissolution of the mixed phase of L1_2 and D0_{22} (Ni_3Al and Ni_3V) was slightly observed at the initial stage (24 hours). At the immersion time of 96 hours, its preferential dissolution became significant. Furthermore, it was found that an intergranular attack was not observed on both compounds, although the attack was observed at $\text{Ni}_3(\text{Si},\text{Ti})$ in HCl solution in previous work [19].

Figure 6 shows the surface morphologies of type 1 and type 2 at the immersion times of 24 hours and 96 hours in the H_2SO_4 solution. The results were almost similar to those in Figure 5. Furthermore, Figure 7 shows the surface morphologies of type 1 and type 2 at the immersion times of 24 hours and 96 hours in the HNO_3 solution. Although the morphologies were similar to those in the HCl and H_2SO_4 solutions, especially for type 2, the degree of corrosion was larger than that in the HCl and H_2SO_4 solutions, in a sense that a dissolution of the L1_2 phase appeared to occur clearly in the HNO_3 solution as well as the development of the preferential dissolution for the mixed phase of L1_2 and D0_{22} (Ni_3Al and Ni_3V), especially compared to those in the HCl solution.

3.4. The Effect of Vanadium on Corrosion Resistance of $\text{Ni}_3\text{Al}/\text{Ni}_3\text{V}$ Two-Phase Intermetallic Compounds. From the above results on type 1 and type 2, it was found that (1) the weight loss increased in order of $\text{HNO}_3 > \text{H}_2\text{SO}_4 > \text{HCl}$

solutions, (2) the preferential dissolution of the mixed phase of L1_2 and D0_{22} (Ni_3Al and Ni_3V) took place, and (3) type 2 containing the minor elements showed a higher corrosion resistance than type 1 without them in HNO_3 solution. These three points would be explained as follows.

Schlain et al. [20] reported that a high purity vanadium (99.9%) was highly resistive to corrosion in H_3PO_4 , H_2SO_4 , and HCl solutions at 35°C , but corroded rapidly in HNO_3 solution. The corrosion of vanadium would explain the above points. Since the corrosion behavior of type 1 and type 2 including vanadium should be reflected by that of the bulk vanadium in the present solutions (point 1), vanadium was present only in the mixed phase (point 2), and the amount of vanadium in type 2 was smaller than that in type 1 (point 3).

For the effect of the minor elements on corrosion resistance, we tried to observe the distribution of the minor elements using electron probe microanalyzer (EPMA). It was found that the distribution appeared to be uniform, showing little enrichment of the minor elements in either the L1_2 phase or the mixed phase. This result would come from the fact that as shown in Figure 1, their microstructures were very fine with several hundreds nm diameter [21], and thus it was difficult to determine the enrichment site. Therefore, the difference in the corrosion resistance between type 1 and type 2 could not be explained only by the influence of minor elements. In addition, type 1 and type 2 showed the higher corrosion resistance in the HCl solution compared to $\text{Ni}_3(\text{Si},\text{Ti})$ and type 304. This suggests that the addition of

vanadium would inhibit the corrosion of type 1 and type 2 in the HCl solution and, however, enhance the corrosion in the H₂SO₄ and HNO₃ solutions. However, to clarify the effect of vanadium, further experiments must be conducted.

4. Conclusion

The corrosion behavior of the Ni₃Al/Ni₃V two-phase intermetallic compounds without the minor elements (type 1) and with them (type 2) in HCl, H₂SO₄, and HNO₃ solutions with 0.5 kmol/m³ has been studied and compared with that of the L1₂ single-phase Ni₃(Si,Ti) and austenitic stainless steel type 304. The following conclusions were obtained.

- (1) The type 1 and type 2 showed the higher corrosion resistance in HCl solution and the lower corrosion resistance in HNO₃ solution than Ni₃(Si,Ti) and type 304 in HCl and H₂SO₄ solutions.
- (2) Both type 1 and type 2 had the preferential dissolution of the mixed phase of L1₂ and D0₂₂ took place in all acidic solutions.
- (3) It was found that the corruptions of type 1 and type 2 were enhanced by the addition of vanadium in HNO₃ solution, while they were inhibited by vanadium in HCl solution.

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