Galvanic Corrosion Behavior of Orthodontic Archwire Alloys Coupled to Bracket Alloys

Masahiro Iijima[a]; Kazuhiko Endo[b]; Toshihiro Yuasa[c]; Hiroki Ohno[d]; Kazuo Hayashi[e]; Mitsugi Kakizaki[f]; Itaru Mizoguchi[g]

ABSTRACT

The purpose of this study was to provide a quantitative assessment of galvanic corrosion behavior of orthodontic archwire alloys coupled to orthodontic bracket alloys in 0.9% NaCl solution and to study the effect of surface area ratios. Two common bracket alloys, stainless steels and titanium, and four common wire alloys, nickel-titanium (NiTi) alloy, β-titanium (β-Ti) alloy, stainless steel, and cobalt-chromium-nickel alloy, were used. Three different area ratios, 1:1, 1:2.35, and 1:3.64, were used; two of them assumed that the multibracket appliances consists of 14 brackets and 0.016 inch of round archwire or 0.016 × 0.022 inch of rectangular archwire. The galvanic current was measured for 3 successive days using zero-impedance ammeter. When the NiTi alloy was coupled with Ti (1:1, 1:2.35, and 1:3.64 of the surface area ratio) or β-Ti alloy was coupled with Ti (1:2.35 and 1:3.64 of the surface area ratio), Ti initially was the anode and corroded. However, the polarity reversed in 1 hour, resulting in corrosion of the NiTi or β-Ti. The NiTi alloy coupled with SUS 304 or Ti exhibited a relatively large galvanic current density even after 72 hours. It is suggested that coupling SUS 304-NiTi and Ti-NiTi may remarkably accelerate the corrosion of NiTi alloy, which serves as the anode. The different anode-cathode area ratios used in this study had little effect on galvanic corrosion behavior.

KEY WORDS: Galvanic corrosion; Archwire; Bracket

INTRODUCTION

Fixed orthodontic metallic appliances such as brackets, archwires, and molar bands are manufactured from base metal alloys such as stainless steel, cobalt-chromium-nickel (CoCrNi) alloy, nickel-titanium (NiTi) alloy, β-titanium (β-Ti) alloy, and pure titanium.[1] These orthodontic alloys, except for β-Ti alloy and pure titanium, contain nickel, and nickel produces more allergic reactions during orthodontic treatment than any other metal.[2–5] Because the release of nickel ions from orthodontic alloys is a clinical concern, general corrosion resistance of orthodontic metal has been widely investigated by many researchers.[6–10]

In a clinical situation, two dissimilar alloys having different corrosion potentials are often placed in contact such as in orthodontic brackets and archwires. This can cause galvanic corrosion that leads to preferential release of metal ions from the anodic metal or alloy.[11–14] Furthermore, the surface area ratio of the two dissimilar alloys is a very important factor because it affects the galvanic corrosion behavior.[11–14] An unfavorable area ratio, which consists of a large cathode and a small anode, might lead to a greater corrosion rate from the anodic alloy.[11] It is also difficult to determine the real surface area ratio between brackets and archwire in clinical use, which has not been performed in previous studies.

The purpose of this study was to provide a quanti-

[a] Assistant Professor, Department of Orthodontics, Health Sciences University of Hokkaido, Hokkaido, Japan.

[b] Associate Professor, Department of Dental Materials Science, Health Sciences University of Hokkaido, Hokkaido, Japan.

[c] Postgraduate Student, Department of Orthodontics, Health Sciences University of Hokkaido, Hokkaido, Japan.

[d] Professor, Department of Dental Materials Science, Health Sciences University of Hokkaido, Hokkaido, Japan.

[e] Instructor, Department of Orthodontics, Health Sciences University of Hokkaido, Hokkaido, Japan.

[f] Dental Technician, School of Dentistry, Health Sciences University of Hokkaido, Hokkaido, Japan.

[g] Professor, Department of Orthodontics, Health Sciences University of Hokkaido, Hokkaido, Japan.

Corresponding author: Masahiro Iijima, DDS, PhD, Department of Orthodontics, School of Dentistry, Health Sciences University of Hokkaido, Kanazawa 1757, Ishikari-Tobetsu, Hokkaido 061-0293, Japan (e-mail: iijima@hoku-iro-u.ac.jp)

TABLE 1. Compositions (Mass %) of Each Alloy[a]

	Ni	Ti	Fe	Cr	Mo	Mn	Co	Zr	Sn	other
Stainless steel (SUS 304)	8.05	—	balance	18.02	—	0.82	—	—	—	<0.604
Titanium (ASTM grade2)	—	balance	—	—	—	—	—	—	—	<0.63
NiTi alloy	55.5	44.1	—	—	—	—	—	—	—	<0.3
Co Cr Ni alloy	15.0	—	15.8	20.0	7.0	2.0	40.0	—	—	<0.19
β-titanium alloy	—	balance	—	—	11.3	—	—	6.6	4.3	<0.3

[a] NiTi indicates nickel-titanium; Co Cr Ni, cobalt-chromium-nickel.

tative assessment of the galvanic corrosion behavior of orthodontic archwire alloys coupled to orthodontic bracket alloys in 0.9% NaCl solution and to study the effect of surface area ratios. The hypotheses in this study were that (1) different kinds of coupled alloys have different galvanic corrosion behavior variants and (2) the surface area ratio affects the galvanic corrosion behavior.

MATERIALS AND METHODS

In this study, two common bracket alloys, stainless steels (Daido Steel, Nagoya, Japan; SUS 304) and titanium (KOBELCO, Hyogo, Japan; ASTM Grade 2), were used. The stainless steel (SUS 304) and titanium (Ti) were rolled sheets and were cut into disk-shaped samples. Four common archwire alloys, NiTi alloy (Ormco, Calif), SUS 304, cobalt-chromium-nickel alloy (Elgiloy blue, Rocky Mountain Orthodontics, Colo), and β-titanium alloy (TMA wire, Ormco), were used. The NiTi was a wiredrawing sample with an approximately 8 mm diameter that was cut into disks of 2 mm thickness. The CoCrNi alloy and β-Ti were the archwire products, and the disk-shaped samples were obtained by casting with an arc-melting gas pressure casting machine under an argon atmosphere (Vulcan-T, Shofu Inc, Kyoto, Japan). The nominal compositions for these alloys are shown in Table 1.

Estimation of the ratio of the brackets and archwire area

Three-dimensional computed models of the brackets (Metal Bracket, Dentsply Sankin, Tokyo, Japan) were constructed on the basis of each exact design drawing, as provided by the manufacture. The surface areas of the brackets were calculated using a computer-aided data analysis system, which consisted of a graphical workstation (Zx1, Intergraph, Huntsville, Ala), and data-processing and data-analyzing software (I-DEAS, SDRC, Milford, Conn) (Table 2). To minimize the computation error, the base plane of the bracket was deleted from the calculated results. Table 3 shows the total surface areas of the brackets and archwires.

The lengths of the archwires were 115 mm for the mandibular arch and 123 mm for the maxillary arch,

TABLE 2. The Surface Area of Each Bracket and Molar Tube (mm²)

Upper central incisor	35.52
Upper lateral incisor	32.00
Lower incisor	28.84
Canine	35.17
Premolar	33.08
First molar	65.85
Second molar	43.86

**TABLE 3.** Total Surface Area of the Brackets, Molar Tube, and Archwires (mm²)[a]

Bracket	
Upper	579.16
Lower	559.48
Molar tube	
Upper (0.016 inch)	237.89
Lower (0.016 inch)	222.45
Archwire	
Upper (0.016 × 0.022 inch)	157.22
Lower (0.016 × 0.022 inch)	147.01

[a] Total surface area of each side were consisted of 10 brackets and four molar tubes. To estimate total area of archwires, 115mm for mandibular arch and 123mm for maxillary upper were used in this study.

and the archwire surface areas were calculated using the value of the cross section claimed by the manufacturer. In this study, three kinds of area ratio, 1:1, 1:2.35, and 1:3.64, were used, and two of them (1:2.35 and 1:3.64) assumed that the multibracket appliances consist of 14 brackets and 0.016 inch (0.41 mm) of round archwire or 0.016 × 0.022 inch (0.41 × 0.56 mm) of rectangular archwire.

Specimen preparation

Specimens of alloys were disk shaped. Three different diameters, 7.5, 11.5, and 14.3 mm, for bracket alloys and one diameter, 7.5 mm, for archwire alloy were used in this study to obtain three area ratios. After specimens were encapsulated in epoxy resin, one side of the surface was polished mechanically to a mirrorlike finish using silicone carbide paper followed by 0.05-μm alumina paste.
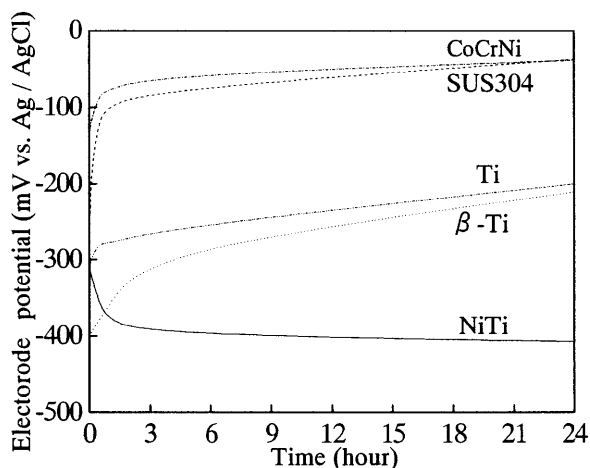
FIGURE 1. Representative corrosion potential of the NiTi, β-Ti, SUS 304, and Ti during the first 24 hours of immersion in 0.9% NaCl solution. NiTi indicates nickel-titanium; β-Ti, β-titanim.

FIGURE 2. Representative galvanic current density of archwire alloys (NiTi, β-Ti, SUS 304, CoCrNi) coupled with bracket alloys (SUS 304, Ti) with area ratio of 1:1 in 0.9% NaCl solution. NiTi indicates nickel-titanium; β-Ti, β-titanim; and CoCr, cobalt-chromium.
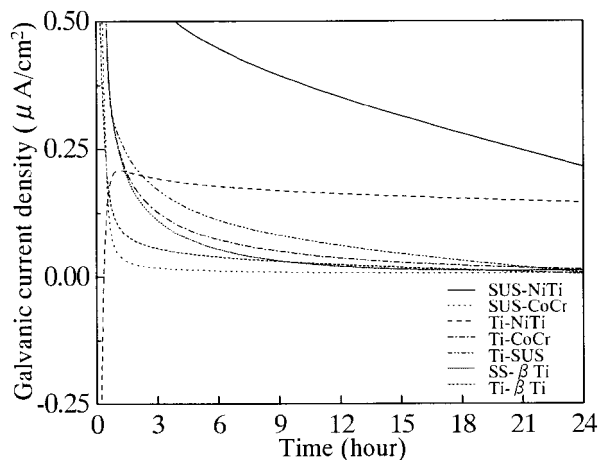
Evaluation of corrosion potential for uncoupled alloys and galvanic corrosion for coupled alloys

The measurement of the potential difference between a working electrode (sample) and a reference electrode is performed with a voltmeter, which should be allowed as little current as possible. This is achieved by having an extremely high internal resistance within the voltmeter.[15]

In this study, the corrosion potentials (E_{corr}) of the uncoupled alloys were measured for three successive days using an electrometer with an input impedance of $10^{12}\Omega$. An Ag/AgCl electrode (saturated KCl) was used as the reference electrode. The electrolyte, 0.9% NaCl solution, was exposed to air and the temperature was kept at 37°C during the experiments. The use of ammeters in galvanic corrosion current measurements should always be treated with caution because their finite resistance adds to the resistance within the corrosion cell and can affect the reactions, which occur. Instruments known as zero-resistance ammeters are used for accurate measurements.[15] In this study, the galvanic current between seven different coupled alloys (SUS 304-NiTi, SUS 304-β-Ti, SUS 304-CoCrNi, Ti-NiTi, Ti-β-Ti, Ti-SUS 304, and Ti-CoCrNi) was measured for 3 successive days using zero-impedance ammeter (2090, Toho Technical Research, Tokyo, Japan). The distance between the two specimens was approximately 10 mm. A total of three replicate samples were investigated both in the corrosion potential measurement for uncoupled alloys and in the galvanic current measurement for coupled samples.

RESULTS

Figure 1 shows the variations in the corrosion potentials (E_{corr}) of representative uncoupled alloys dur-

ing the first 24 hours of immersion in 0.9% NaCl solution. The corrosion potentials (E_{corr}) of the uncoupled β-Ti, CoCrNi, SUS 304, and Ti moved in the noble direction a few hours after starting immersion, whereas the corrosion potential of the NiTi moved in the less noble direction a few hours after starting immersion. Comparing the steady-state values of E_{corr}, SUS 304 and CoCrNi indicated more noble corrosion potential (approximately −50 mV for both samples) than any other samples. In contrast, the corrosion potential for the NiTi (approximately −400 mV) was much lower than that for any other samples. The corrosion potentials obtained from Ti and β-Ti (approximately −200 mV) were intermediate.

The galvanic current density was calculated from the measured galvanic current and surface area of the alloy, which served as an anode during most of the measurement time. Figures 2 through 4 show the variation in the galvanic current density during the first 24 hours of immersion; similar results were found for second and third samples. Table 4 shows the mean values of the galvanic current density obtained from all coupled alloys at 24, 48, and 72 hours. In all coupled samples, the galvanic current density decreased with time and reached a nearly constant value after 24 hours. In NiTi alloy coupled with Ti (1:1, 1:2.35, and 1:3.64 of the surface ratio) or β-Ti alloy coupled with Ti (1:2.35 and 1:3.64 of the surface ratio), Ti was initially the anode and corroded. However, the polarity reversed in 1 hour, resulting in corrosion of the NiTi or β-Ti. The galvanic current density for NiTi alloy coupled with SUS 304 or Ti at 72 hours of immersion was 0.033 to 0.114 $\mu A/cm^2$, which was more than one order of magnitude higher than that observed for the other couples.
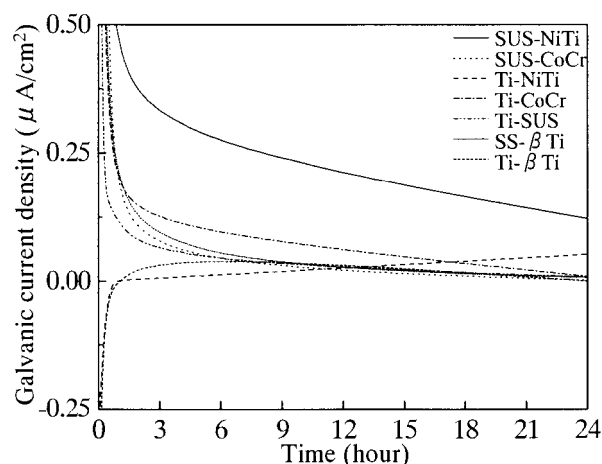
FIGURE 3. Representative galvanic current density of archwire alloys (NiTi, β-Ti, SUS 304, CoCrNi) coupled with bracket alloys (SUS 304, Ti) with area ratio of 1:2.35 during the first 24 hours of immersion in 0.9% NaCl solution. NiTi indicates nickel-titanium; β-Ti, β-titanim; and CoCr, cobalt-chromium.
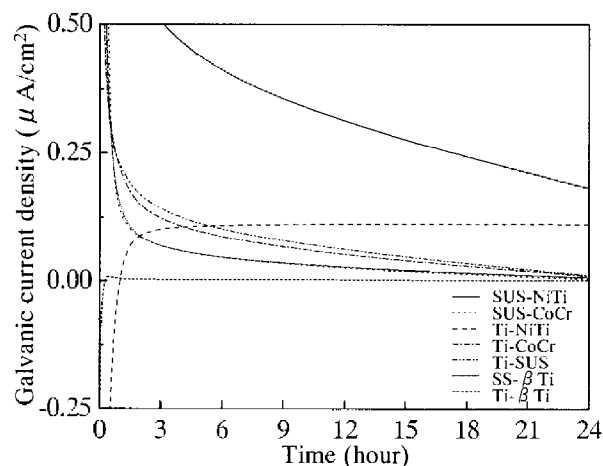
FIGURE 4. Representative galvanic current density of archwire alloys (NiTi, β-Ti, SUS 304, CoCrNi) coupled with bracket alloys (SUS 304, Ti) with area ratio of 1:3.64 during the first 24 hours of immersion in 0.9% NaCl solution. NiTi indicates nickel-titanium; β-Ti, β-titanim; and CoCr, cobalt-chromium.

DISCUSSION

This study focused on galvanic corrosion behavior for orthodontic archwire alloys coupled to orthodontic bracket alloys with different compositions using disk-shaped specimens with relatively similar surface conditions. All specimens were polished mechanically to a mirrorlike finish to minimize the difference of specimen surface conditions such as surface roughness and the structure of the surface oxide film. Also, the adjustment of the surface area was easier by using disk-shaped specimens.

The starting point for the manufacturing of orthodontic wires is the casting of an ingot having the appropriate alloy composition.[1] This ingot is subjected to a series of mechanical reduction operations until the cross section is sufficiently small for wiredrawing, and then, the wiredrawing is performed.[1]

Heat treatments are necessary during wire manufacturing to eliminate the extensive work hardening, which occurs during the various stages of mechanical reduction.[1] Previous study has demonstrated that the oxide film on the commercial NiTi orthodontic wire,

TABLE 4. Mean Galvanic Current Density at 24, 48, and 72 h (μA/cm²)[a]

Area Ratio	Coupled Alloys	Mean (Range) at 24 h	Mean (Range) at 48 h	Mean (Range) at 72 h
1:1	SUS-NiTi	0.156 (0.095–0.214)	0.081 (0.064–0.1)	0.114 (0.052–0.215)
	SUS-CoCr	0.001 (0–0.001)	0.001 (0–0.002)	0.003 (0–0.007)
	SUS-β-Ti	0.007 (0.004–0.011)	0.002 (0.002–0.003)	0.005 (0.001–0.012)
	Ti-NiTi	0.138 (0.064–0.269)	0.066 (0.048–0.095)	0.076 (0.039–0.145)
	Ti-CoCr	0.004 (0–0.007)	0.003 (0–0.007)	0.005 (0–0.014)
	Ti-SUS	0.005 (0–0.010)	0.004 (0–0.011)	0.003 (0–0.007)
	Ti-β-Ti	0.001 (0–0.0023)	0 (0–0.001)	0.003 (0–0.005)
1:2:35	SUS-NiTi	0.0714 (0.034–0.121)	0.055 (0.025–0.096)	0.044 (0.020–0.077)
	SUS-CoCr	0.001 (0.001–0.002)	0 (0–0)	0 (0–0.002)
	SUS-β-Ti	0.005 (0.003–0.007)	0.003 (0.002–0.004)	0.003 (0.001–0.007)
	Ti-NiTi	0.041 (0.023–0.062)	0.033 (0.019–0.051)	0.033 (0.017–0.062)
	Ti-CoCr	0.008 (0.006–0.010)	0.004 (0.002–0.006)	0.004 (0.002–0.006)
	Ti-SUS	0.007 (0.005–0.009)	0.003 (0.03–0.003)	0.003 (0.003–0.005)
	Ti-β-Ti	0.001 (0.001–0.001)	0 (0–0)	0 (0–0)
1:3:64	SUS-NiTi	0.083 (0.055–0.121)	0.081 (0.042–0.129)	0.068 (0.035–0.109)
	SUS-CoCr	0.001 (0.001–0.002)	0.006 (0.003–0.011)	0.005 (0.001–0.009)
	SUS-β-Ti	0.005 (0.003–0.007)	0.004 (0.002–0.005)	0.002 (0.001–0.003)
	Ti-NiTi	0.066 (0.049–0.100)	0.081 (0.047–0.119)	0.071 (0.042–0.104)
	Ti-CoCr	0.010 (0.006–0.015)	0.005 (0.003–0.008)	0.004 (0.002–0.006)
	Ti-SUS	0.012 (0.005–0.017)	0.006 (0.005–0.008)	0.005 (0.003–0.008)
	Ti-β-Ti	0.001 (0.001–0.001)	0 (0–0)	0 (0–0)

[a] NiTi indicates nickel-titanium alloy; CoCr, cobalt-chromium alloy; and β-Ti, β-titanium alloy.

formed by wire manufacturing processes such as heat treatment and pickling, causes an increase in the corrosion resistance. When this occurs, the amount of released metal ions from the commercial NiTi orthodontic wire was lower than that from the disk-shaped specimen with a polished surface in 0.9% NaCl solution.[7] In another previous study that measured the free corrosion potential in the 0.9% NaCl solution for commercial orthodontic brackets, orthodontic archwire, and coil springs demonstrated that the two piece type brackets made by soldering or welding had a remarkably lower corrosion potential value in comparison with one piece type brackets because the contact point between the wing and the base might be a susceptible site for localized corrosion.[16] Consequently, corrosion behavior of wrought orthodontic brackets and orthodontic archwire with various surface conditions in the real oral environment should be extremely complex and may differ slightly from the results obtained in this study, which used disk-shaped specimens with polished surfaces. However, the tendency of both galvanic corrosion behaviors obtained from disk-shaped specimens with polished surface and that obtained from wrought orthodontic brackets and orthodontic archwires should be similar.

In electrochemical corrosion, a galvanic cell is created when two different metals, or different areas on the same metal, are coupled. In galvanic corrosion, some current flows between the anodic and the cathodic areas situated at different parts of a metallic surface or between different metals of the same or different materials. The driving force for corrosion is a potential difference between the different materials.

Clinically, mixed alloys having different corrosion potentials are often placed in contact in the oral environment, as with orthodontic brackets and archwires. This can cause galvanic corrosion that leads to preferential release of metal ions from the anodic alloy.[11–14] Another clinically important example of this phenomenon is the concentration cell corrosion that takes place under the oral debris covering a pit on a metallic appliance. Because of the lower concentration of oxygen compared with the bulk oral environment, a rapid attack occurs at the bottom of the pit.[17] The multiplied effect of concentration cell corrosion and galvanic corrosion may accelerate corrosion behavior remarkably.

In this study, the galvanic current decreased with time and reached a nearly constant value after 24 hours for all coupled samples (Figures 2 through 4). In NiTi alloy coupled with Ti (1:1, 1:2.35, and 1:3.64 of the surface ratio), Ti was initially anode and corroded; however, the polarity reversed in 1 hour, resulting in corrosion of the NiTi. This phenomenon can be explained by the time change of corrosion potential (E_{corr}) because the corrosion potential of the Ti was lower than that of NiTi immediately after starting immersion and moved in the noble direction in a few hours. On the other hand, the corrosion potential of the NiTi moved in the less noble direction after the starting immersion (Figure 1).

A previous study using X-ray photoelectron spectroscopy (XPS) demonstrated that the thickness of the surface films formed on titanium specimens immersed in electrolyte solutions (pH 4.5, 5.2, 7.4) at 37°C increased during immersion.[18] Similarly, the surface oxide film of Ti, which mainly is composed of TiO_2, was probably aged along with increasing the thickness of the surface oxide film in this study. The result of this was that the corrosion potential of the Ti moved in the noble direction. Another previous study also demonstrated the surface oxide film of the commercial orthodontic NiTi wire aged in the 0.9% NaCl solution and the thickness of the oxide film increased during immersion in the 0.9% NaCl solution.[7] However, the corrosion potential of the NiTi moved in the less noble direction after starting immersion in this study. The XPS demonstrated that the NiTi alloy surface under the passive film was rich in Ni because of a preferential oxidation of Ti.[7] The enrichment of Ni at the alloy/oxide film interface may be related to the decrease in corrosion potential. Further research is necessary to study more details of these contradictory phenomena.

The galvanic current density for NiTi alloy coupled with SUS 304 or Ti at 72 hours of immersion was 0.033 to 0.114 $\mu A/cm^2$, which was more than one order of magnitude higher than that observed for the other couples. The reason for this is that there were relatively large differences in the corrosion potentials (E_{corr}) between the NiTi alloy and the other two alloys in the uncoupled sample. The corrosion rate of uncoupled NiTi in the 0.9% NaCl solution could be approximated from the amount of nickel ions released into the solution using Faraday's law. The average corrosion rate during 28 days thus estimated was 0.54 nA/cm^2.[10] However, the galvanic current density obtained in this study at 72 hours of immersion was found to be increased from approximately 80 to 210 times when the NiTi was galvanically coupled with SUS 304 or Ti. It is suggested that coupling SUS 304-NiTi and Ti-NiTi may remarkably accelerate the corrosion of NiTi alloy, which serves as the anode.

The surface area ratio of two dissimilar alloys is an extremely important factor because it affects the galvanic corrosion behavior.[11,13,14] An unfavorable area ratio, which consists of a large cathode and a small anode, might lead to the greater corrosion rate of the anodic alloy,[11] possibly causing problems if the anodic alloy contained a high-risk element such as nickel.

This study used a computer-aided data analysis system to estimate the surface area of the brackets

accurately. The results obtained show that differing surface area ratios of two dissimilar alloys had little effect on galvanic corrosion behavior. This is in agreement with another recent study that compared corrosion rates of three different ratios of surface areas between 2205 stainless steel, which is a dual phase stainless steel, and SUS 316L.[11]

Figure 5 illustrates the effect of anode-cathode area ratio on the anodic and cathodic polarization curves for (1) an actively corroding alloy and (2) a passive alloy when each alloy is galvanically coupled to an alloy that has more positive potential (cathodic). When equal areas of the anodic and cathodic alloys are coupled, the corrosion rate of the active and the passive alloys are I_{corr}, a_1 and I_{corr}, p_1, respectively. The corrosion rate of the active alloy is increased from I_{corr}, a_1 to I_{corr}, a_2 as the area of cathodic alloy is increased from S to 3.64S. In contrast to this, the corrosion current of the passive alloy is not markedly influenced by the surface area of the cathodic alloy because the anodic current of the passive alloy is almost constant, independent of potential in the passive region. Because the alloys used in this study were all passive, the surface area ratio of two dissimilar alloys had little effect on the corrosion rate, as shown in Figure 5b.

Although polished disk-shaped specimens were used for brackets and archwire alloys in this study, commercial archwires have a thick oxide film of approximately two nm thickness on the surface as a result of the production processes, such as the heat treatment and pickling processes. This causes an increase in both the general and the localized corrosion resistance.[7,10] Furthermore, the surface of the brackets and archwires could be scratched by bending and ligating clinically. Thus, further investigations are required to determine the galvanic corrosion behavior in clinical applications.

CONCLUSIONS

- In NiTi alloy coupled with Ti for all the surface ratio (1:1, 1:2.35, and 1:3.64), Ti was initially anode and corroded; however, the polarity reversed within one hour, resulting in corrosion of NiTi.
- It is suggested that coupling SUS 304-NiTi and Ti-NiTi may remarkably accelerate the corrosion of NiTi alloy, which served as the anode, because NiTi alloy coupled with SUS 304 or Ti exhibited more than one order of magnitude higher than that observed for the other couples at 72 hours of immersion.
- The different anodic-cathodic area ratios used in this study (1:1, 1:2.35, and 1:3.64) had little effect on galvanic corrosion behavior.
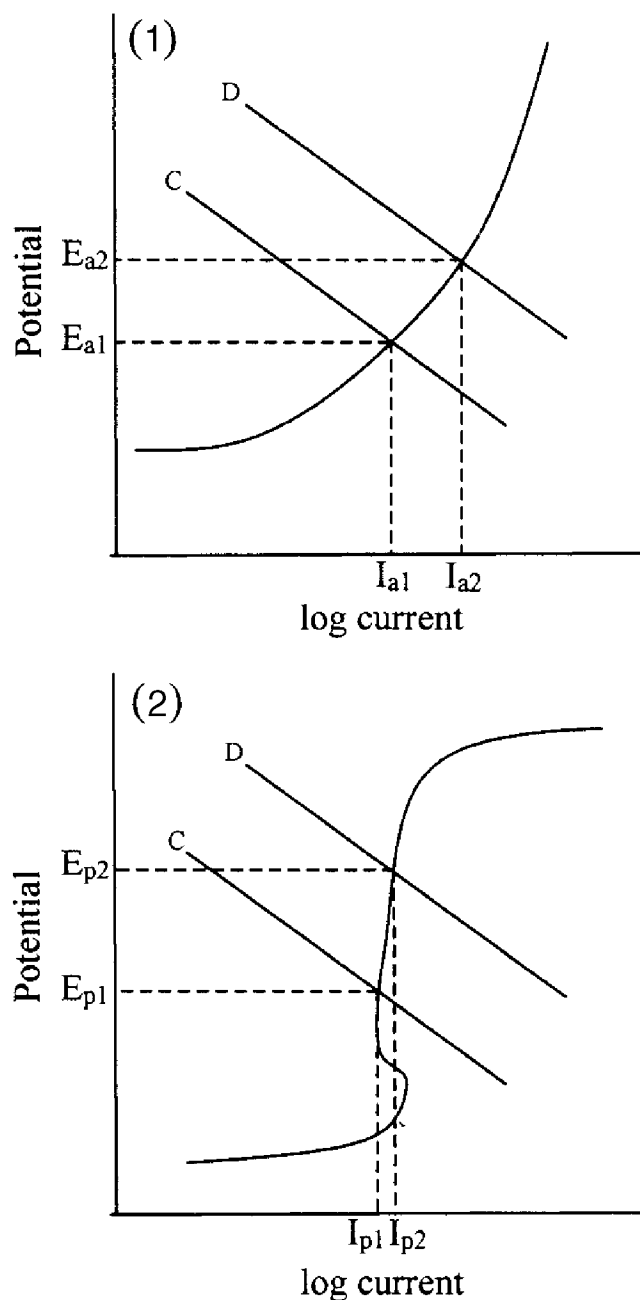
FIGURE 5. Effect of anode-cathode area ratio on the polarization diagram of two galvanically coupled alloys. (A) Anodic polarization curve of an active alloy with surface area of S cm². (B) Anodic polarization curve of a passive alloy with surface area of S cm². (C) Cathodic polarization curve when each alloy is coupled to an alloy (S cm²) with relatively noble potential. (D) Cathodic polarization curve when each alloy is coupled to an alloy (3.64 cm²) with relatively noble potential.

ACKNOWLEDGMENTS

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