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Corrosion of Orthodontic Wires According to Heat Treatment Conditions

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Heat treatments are applied to orthodontic wires in order to relieve the stresses arising during orthodontic work. Four types of wires were heated in air, argon or vacuum environments, and cooled in the furnace or in a water bath. The susceptibility to corrosion and mechanical properties of the heat-treated wires were investigated. Heat treatment marginally increased the yield strength and elastic modulus of all wires. After heat treatment in air, both water- and furnace-cooled wires had similar low corrosion resistances. Corrosion resistances of wires heated under vacuum differed significantly according to cooling methods, such that furnace-cooled wires had higher corrosion resistances than water-cooled wires. Water-cooled wires consistently showed low corrosion resistance whether heated in vacuum, argon, or air environments. After heat treatment under vacuum, furnace-cooled wires had low current densities and high pitting potentials similar to control wires, but other heat-treated wires generally exhibited high current densities and low pitting potentials. Wires heat-treated under vacuum or argon and then cooled in the furnace were the least susceptible to surface oxidation and corrosion, and showed a marginal improvement in mechanical properties. Therefore, we conclude that wires treated in these way can reduce metal ion release and wire fracture, which can minimize adverse effects arising from orthodontic practices.

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1. Introduction

Orthodontic wires are used with brackets to apply biomechanical forces that affect tooth movement. Therefore, the orthodontist should consider many factors, such as the amount of applied force that is desired, the working range or springback, the formability or ease of manipulation, and the need for soldering or welding to assemble an appliance. *In vivo* corrosion, the release of metal ions, and the ensuing biocompatibility concerns are also important factors.[1)]

Because stainless steel wires undergo cold working processes such as rolling, pressing and drawing, and are deformed plastically by the orthodontist's manipulations, internal stresses build up in the wire. That can alter its elasticity and mechanical properties. To relieve these stresses, wire loops, helical springs, or archforms, are annealed by heat treatment after formation. Although annealing improves elasticity, removes dislocations, and restores shape,[2)] it can reduce the resistance of wires to corrosion by surface oxidation and contamination.[3)] The release of corroded material and metal ions into the oral cavity can cause significant health problems.

Toms[4)] reported that, the corrosion of orthodontic appliances could have serious clinical implications, including alterations in size and shape that can reduce the force applied to teeth, and the release of potentially toxic corrosion products. Barrett *et al.*[5)] reported the release of nickel and chromium ions from orthodontic appliances by *in vitro* test, and Bishara *et al.*[6)] observed increases in the concentration of nickel in the blood caused by the biodegradation of orthodontic appliances. Bass *et al.*[7)] observed upon nickel hypersensitivity in orthodontic patients. From these findings, it is of considerable clinical importance that the corrosion behavior of orthodontic wires are characterized. Although the corrosion of orthodontic appliances has been widely studied, only the study of Toms *et al.*[4)] has investigated the corrosion behavior of heat-treated wires. This study showed wires heat-treated at low temperature (400°C) for 10 min had increased corrosion resistance. Therefore, the objectives of the present study were to determine the effects of both heat treatment environment and cooling method on the susceptibility of wires to corrosion and to suggest a heat treatment protocol to maximize their resistance to corrosion as well as their mechanical advantages.

2. Materials and Methods

Four types of orthodontic stainless steel wires were investigated: Remanium (Dentaurum, Ispringen, Germany), Permachrome (3M Unitek, Monrovia, USA), Colboloy (G&H, Greenwood, USA), and Orthos (Ormco, Glendora, USA). The chemical compositions of these wires are shown in Table 1. All products were supplied as straight lengths with cross sections of 0.41 mm × 0.56 mm. Stress relief heat treatment was performed in a furnace at 500°C for 6 min in a vacuum (at ca. 1.33×10^{-3} Pa), or in air or argon environments (above 1.01×10^{5} Pa). Wires were allowed to cool either in the furnace or in a water bath. The heating rate was 10°C/min and the cooling rate about 3–5°C/min in the furnace. 'As received' wires were used as controls.

A three point bending test was carried out to evaluate the mechanical properties of the heat-treated wires. The test was performed at a crosshead speed of 5 mm/min and a full-scale load range of 10 kgf, using a tensile test machine (Series IX

Table 1 Chemical composition (%) of the orthodontic wires.

Specimen	Fe	Cr	Ni	Si	C	S
Remanium	71.25	18.75	8.29	1.13	0.11	0.006
Permachrome	69.17	19.92	9.00	1.56	0.08	0.003
Colboloy	70.42	19.71	8.65	0.79	0.08	0.002
Orthos	66.68	19.45	8.79	1.77	0.08	0.004

Table 2 Constituents of artificial saliva.

Constituent	Concentration (g/L)
NaCl	0.40
KCl	0.40
$CaCl_2 \cdot 2H_2O$	0.795
$NaH_2PO_4 \cdot 2H_2O$	0.780
$Na_2S \cdot 9H_2O$	0.005
$CO(NH_2)_2$(Urea)	1.0
Distilled water	1 L

Automated Materials Testing System, Instron Corp., Carrtorr, USA). Bending yield strength (0.2% offset), and Young's modulus were determined in five 7.5 cm-long replicate specimens of each wire.

To investigate the corrosion properties of the heat-treated wires, potentiodynamic testing was performed on 3 cm-long samples in an artificial saliva solution (Table 2) at 37 ± 1°C, using a potentiostat (Model 263A, EG&G Instruments, NJ, USA). Samples for corrosion testing were ultrasonically cleaned in each acetone and ethylalcohol solution for 5 min, rinsed in distilled water, and dried. The potential scanning rate was 60 mV/min, the scanning range was −600 mV–1000 mV, and a saturated calomel electrode (SCE) was used as the reference electrode. To evaluate the corrosion behavior of heat-treated wires, pitting potential and passive current density were measured using an anodic polarization test.

Statistical analyses were performed using Kruskal-Wallis tests, and significant differences were accepted at the 95% confidence interval. Significant differences in bending properties according to heat treatment condition were decided by Scheffe tests.

3. Results

3.1 Bending properties

The effects of heat treatment and cooling method on yield strength and elastic modulus are shown in Tables 3 and 4. Heat-treated wires showed yield strength increases of 3.7–14.4%, and elastic modulus increases of 2.5–9.0%, compared with controls. Small but significant differences were found in the yield strengths of the wires according to heat treatment environment and cooling method. Water-cooled wires had lower yield strengths than furnace-cooled wires. In terms of elastic modulus, wires heat-treated under vacuum showed greater increases than those heated in air or argon, and wires cooled in the furnace.

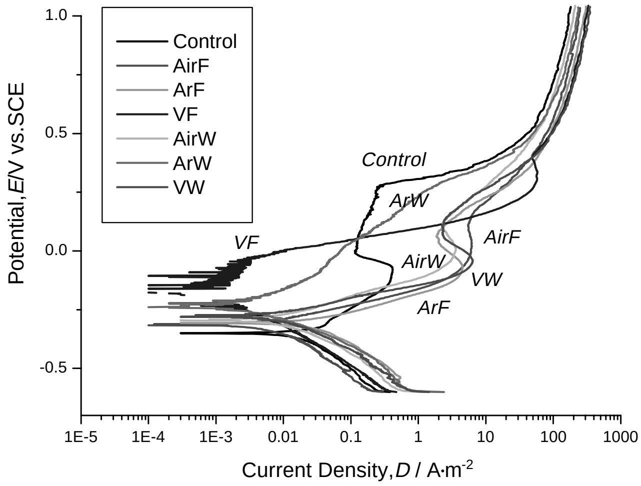

Fig. 1 Anodic polarization curves of Remanium in artificial saliva after different heat treatments.

3.2 Corrosion properties

3.2.1 Remanium:

Anodic polarization curves of furnace- and water-cooled Remanium wires are presented in Fig. 1. Compared with other untreated wires, Remanium had the lowest pitting potential (270 mV (SCE)), the highest passive current density (0.17 $A \cdot m^{-2}$), and the narrowest passive region. Corrosion resistance of Remanium after all heat treatments was decreased compared with the control. Most of the heat-treated Remanium wires showed higher passive current densities in the range of 1.20–5.50 $A \cdot m^{-2}$ at 0.1 V (SCE). Remanium cooled in water after heating in all environments had a relatively high current density that increased linearly with potential (Fig. 1), indicating that corrosion occurred above 0 V (SCE) in artificial saliva. Pitting potential of Remanium could be defined only for anodic polarization curves of the control wire, because the current density of heat-treated wires increased linearly with potential.

3.2.2 Permachrome:

Anodic polarization curves of Permachrome are presented in Fig. 2. The passive current density of the Permachrome control wire was approximately 0.01 $A \cdot m^{-2}$, and that of the wire heat treated under vacuum and cooled in the furnace, 0.002 $A \cdot m^{-2}$. However all other treated Permachrome wires showed high passive current densities in the range of 0.30–3.70 $A \cdot m^{-2}$. Permachrome pitted in the same manner as Remanium. The control wire had a high pitting potential of 320 mV (SCE), and the wire heated under vacuum and cooled in the furnace had a pitting potential of 240 mV (SCE). All other wires had low pitting potentials of less than 200 mV (SCE).

3.2.3 Colboloy:

Anodic polarization curves of Colboloy are presented in Fig. 3. Colboloy control wire showed a relatively high pitting potential of 450 mV (SCE) and a high passive current density of 0.45 $A \cdot m^{-2}$. Anodic polarization curves of heat treated Colboloy showed increased current densities. The passive current density of the wire heated under vacuum and cooled in the furnace was the lowest of all treated wires; Colboloy wires heat treated in air and argon environments showed similar corrosion behavior.

Table 3 Bending yield strength of heat-treated wires.

Sample		Bending yield strength (MPa)		
		Vacuum	Air	Ar
	Control		1094.9 ± 7.4[a]	
Remanium	Water cooling	1202.5 ± 13.0[b]	1183.8 ± 15.0[b]	1228.9 ± 22.2[b]
	Furnace cooling	1193.6 ± 12.5[b]	1227.9 ± 14.4[b]	1222.8 ± 16.7[b]
	Control		1146.2 ± 9.9[a]	
Permachrome	Water cooling	1259.1 ± 9.6[b]	1249.3 ± 13.7[b]	1244.2 ± 2.3[b]
	Furnace cooling	1289.7 ± 8.1[b]	1266.6 ± 9.3[b]	1274.8 ± 13.3[b]
	Control		1122.1 ± 19.1[a]	
Colboloy	Water cooling	1261.1 ± 7.9[bc]	1191.1 ± 15.1[ab]	1221.7 ± 30.0[bc]
	Furnace cooling	1283.4 ± 13.6[c]	1212.5 ± 11.5[abc]	1210.7 ± 10.3[abc]
	Control		1271.6 ± 20.1[a]	
Orthos	Water cooling	1331.3 ± 12.7[b]	1318.7 ± 8.8[b]	1327.5 ± 17.8[b]
	Furnace cooling	1371.4 ± 21.6[b]	1331.8 ± 11.0[ab]	1365.1 ± 26.6[b]

a, b, c: significantly different according to heat treatment conditions ($p < 0.05$).

Table 4 Bending elastic modulus of heat-treated wires.

Sample		Elastic modulus (GPa)		
		Vacuum	Air	Ar
	Control		160.6 ± 0.3[a]	
Remanium	Water cooling	170.9 ± 1.8[b]	167.4 ± 1.0[b]	169.1 ± 0.6[b]
	Furnace cooling	170.0 ± 0.7[b]	168.3 ± 1.6[b]	169.6 ± 0.6[b]
	Control		164.5 ± 0.5[a]	
Permachrome	Water cooling	174.6 ± 0.3[bc]	171.8 ± 0.7[b]	171.0 ± 0.8[b]
	Furnace cooling	176.1 ± 0.8[c]	171.5 ± 0.9[b]	172.1 ± 0.9[b]
	Control		161.8 ± 1.6[a]	
Colboloy	Water cooling	175.9 ± 1.3[c]	165.7 ± 1.5[ab]	170.4 ± 1.5[bc]
	Furnace cooling	176.2 ± 1.2[c]	167.4 ± 0.6[ab]	168.1 ± 0.5[ab]
	Control		171.3 ± 1.5[a]	
Orthos	Water cooling	179.6 ± 0.8[b]	175.9 ± 1.8[bc]	177.9 ± 1.2[b]
	Furnace cooling	182.1 ± 0.8[b]	178.1 ± 0.9[b]	180.5 ± 1.5[b]

a, b, c: significantly different according to heat treatment conditions ($p < 0.05$).

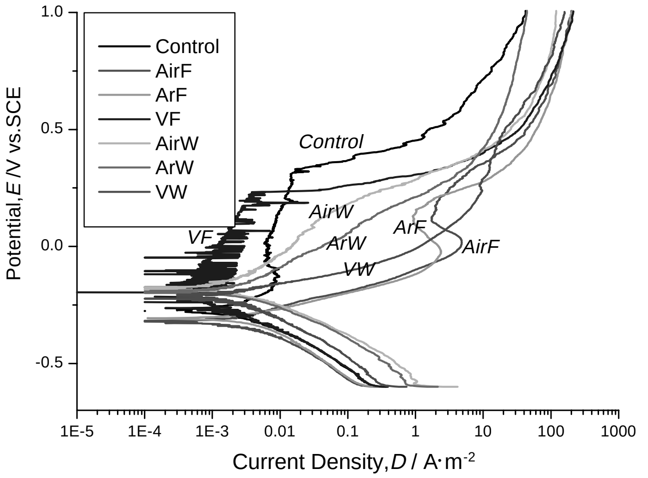

Fig. 2 Anodic polarization curves of Permachrome in artificial saliva after different heat treatments.

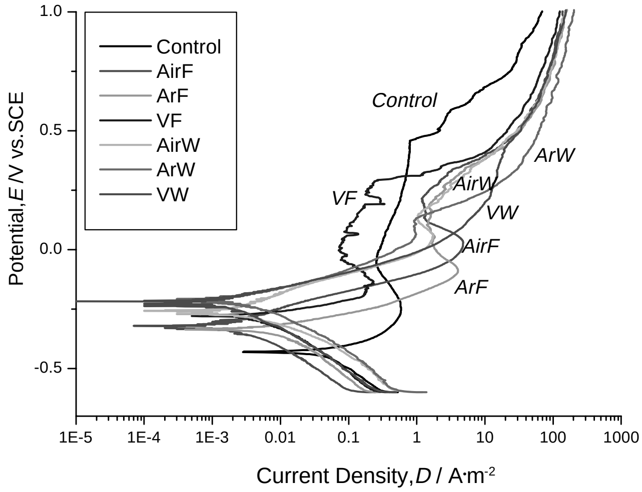

Fig. 3 Anodic polarization curves of Colboloy in artificial saliva after different heat treatments.

3.2.4 Orthos:

The results of anodic polarization tests on Orthos are shown in Fig. 4. The Orthos control showed a passive current density of about 0.048 $A \cdot m^{-2}$ and a pitting potential of about 510 mV (SCE). Passive current density of the wire heat treated under vacuum and cooled in the furnace was the lowest with

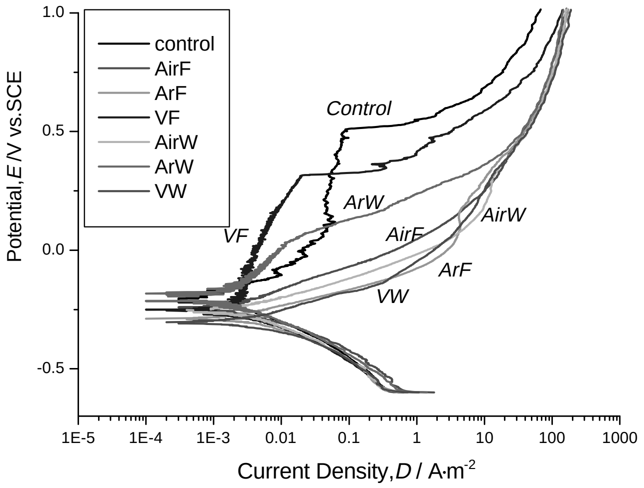

Fig. 4 Anodic polarization curves of Orthos in artificial saliva after different heat treatments.

a value of 0.006 $A\cdot m^{-2}$, pitting potential was approximately 310 mV (SCE), lower than the control. Figure 4 shows that the anodic polarization curves of all wires cooled in water after any heat treatment increased linearly with potential, indicating that corrosion takes place continuously in the case of heat-treated wire with increased potential.

4. Discussion

Many researchers have investigated the corrosion of metallic orthodontic appliances. Although no severe health problems have yet been attributed to the use of such appliances, the potential for health problems due to corrosion of them necessitates continued research.

Although all constituents of orthodontic appliances are generally highly resistant to corrosion when examined singly, the corrosion may nevertheless occur due to interaction for orthodontic treatment in the oral cavity. When a bracket and wire are combined with ligature wire or an elastomeric O-ring, crevice or galvanic corrosion can occur in the oral cavity, and when a bracket is soldered onto a metal band, many types of corrosion can occur. Pitting corrosion may occur on orthodontic appliances by aggressive Cl^- ion attack from saliva or from food or drink. In environments with high chloride concentrations heterogeneous oxygen concentrations, and low pH, passive films of stainless steel tend to be unstable so that pitting and crevice corrosion occur more easily. Similar condition are often found in the oral cavity. Because nickel and chromium ions released by corrosion can induce adverse reactions in the human body, it is important that we try to minimize these corrosion risks.

Nickel and chromium are two metals used in the construction of most orthodontic appliances. The predominant systemic effects of these metals in humans are allergies, dermatitis, and asthma. Nickel is one of the most common causes of allergic contact dermatitis, especially in women.[8] Despite the fact that nickel is used to produce stainless steel alloys, most nickel-sensitive patients are able to tolerate these alloys without difficulty. The crystal lattice of the alloys generally binds the nickel so that it is not free to react. Furthermore, a protective film of stainless steel, called the passive film, can inhibit the release of metallic ions. However, if heat treatment alters this passive layer to become porous or otherwise non-protective, the alloy cannot be protected from corrosion and metallic ions can be released from the wire surface into the oral cavity. Although heat treatment improves the mechanical properties of the wire, it may reduce resistance to corrosion.

Anodic polarization tests showed that the heat treatment environments and cooling methods examined substantially affected pitting potential and passive current density of the wires. Control wires and furnace-cooled wires that had been heat treated under vacuum had high corrosion resistance, but most other heat treated wires had relatively low corrosion resistance. Water-cooled wires were significantly different from furnace-cooled wires after heat treatment under vacuum, in terms of both pitting potential and current density. Water-cooled wires after heat treatment under vacuum or air or argon generally had relatively higher current densities and lower pitting potentials; there were no significant differences between wire types and there was no significant difference between water- and furnace-cooled wires after heat treatment in air in terms of current density. Current densities measured at certain potentials in artificial saliva were dependent on heat treatment environment and cooling method, whether or not a passive region was formed on the wire. The passivity of the wire was dependent on the properties of the film formed by the heat treatment. Control wires and furnace-cooled wires after heat treatment under vacuum contained the passive regions, but all other treatments produced wires with high current densities and without stable passive regions.

In the analysis of anodic polarization curves, a high current density suggests that metallic ions are dissolved in relatively high concentrations due to corrosion reaction rates. Therefore, wires with low current densities are likely to have good corrosion resistance and to inhibit the corrosion reaction in artificial saliva. Stainless steel is protected from corrosion by a stable passive film so that it has good corrosion resistance. However, it is known that type 304 and 302 stainless steels have a low pitting resistance in environments that contain aggressive ions, such as chloride in seawater. In anodic polarization curves, pitting potential is defined as the potential when the current density increases sharply in a passive region. A high pitting potential corresponds to high pitting resistance. The compositions of wires used in the present study (Table 1) indicate that Remanium is a type 302 stainless steel and that other wires are type 304 stainless steels. Various kinds of film can be formed on these steels according to heat treatment conditions. If the heat treatment forms a dense inert film, the matrix can be protected and the pitting potential increased. If the film is rough and not dense, such as the film formed by water cooling after heat treatment in air, the pitting potential may be decreased and the corrosion rate correspondingly increased. Accordingly, it is important to pay attention to the stability of newly formed film as well as to the improvement in mechanical properties of wires in relation to heat treatment temperatures, durations, environments and cooling methods.

Control- and furnace-cooled wires that had been heat treated under vacuum, except for Remanium, showed higher pitting potentials than the redox potential present in the oral cavity[9] (−58 to +212 mV (SCE)). However most other treatments, the pitting potential was lower than the redox potential in the oral cavity. In particular, wires cooled in water showed very high current densities regardless of heat treatment environment, which suggests that water cooling formed an unstable porous film that accelerated the corrosion of the stainless steel wire. Therefore, it is recommended that water cooling should not be used in the preparation of orthodontic appliances.

Oh *et al.*[3] reported that the heat treatment of wires reduced their metallic luster and generally resulted in a straw coloration due to the formation of Fe_2O_3 oxide. However, it is believed that a porous or non-protective oxide layer could increase the risk of localized corrosion. Wires cooled in the furnace after heat treatment under vacuum formed thin and stable films on the surface, but wires cooled in water formed rough and unstable films, firstly because of oxides formed by rapid reaction with oxygen when the wires are removed from the vacuum furnace, and secondly because of hydroxides formed by the reaction with water in the water bath. Therefore, after heat treatment under vacuum, water cooling should not be used. Very little difference in corrosion resistance was found between cooling methods for wires heated in air because of the thick oxide film formed by surface oxidation. In wire heated in argon, slight enhancements in corrosion resistance were found to be dependent upon the type of wire and the cooling method. This result was probably due to the inhibiting effect of argon on surface oxidation. Furnace cooling kept the surface clean and smooth, but water cooling made the surface rough by allowing the formation of oxides and hydroxides. To inhibit surface oxidation and keep the surface clean, orthodontic wires should be heat treated in either a vacuum or an inert gas environment. To prevent corrosion during use, wires should be furnace cooled, and, most importantly, should not be water-cooled.

5. Conclusions

(1) Stress relief heat treatment increased the bending yield strength and Young's modulus of four types of orthodontic wire in the range of 3.7–14.4% and 2.5–9.0%, respectively.

(2) After heat treatment in air, both water- and furnace-cooled wires showed pronounced surface oxidation and had similar low corrosion resistances. Under heat treatment under vacuum, furnace-cooled wires showed significantly higher corrosion resistance than water-cooled wires.

(3) After heat treatment under vacuum, argon, or air environments, water-cooled wires had low corrosion resistance, probably because of the irregular and unstable films formed on the surface of the wires quenched in water.

(4) Control wires and furnace-cooled wires after heat treatment under vacuum showed low current densities and high pitting potentials, but most treated wires showed high current densities and low pitting potentials.

The results of the present study show that orthodontic wires heat treated under vacuum and then cooled in the furnace had reduced surface oxidation and marginally corrosion resistances and improved mechanical properties. Therefore, it is considered that wires treated in this way can reduce adverse effects and wire fracture in the oral cavity.

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