

Corrosion of Ni-Ti Rotary Instruments: A Review

Zahed Mohammadi¹, Jun-Ichiro Kinoshita², Atsufumi Manabe², Mikihiro Kobayashi², Sousan Shalavi³, Hamid Jafarzadeh⁴

¹ Adjunct Clinical Professor of Endodontics, Iranian Center for Endodontic Research (ICER), Research Institute of Dental Sciences, Shahid Beheshti University of Medical Sciences, Tehran, Iran and Iranian National Elites Foundation, Tehran, Iran

² Department of Conservative Dentistry, Showa University Dental Hospital, Tokyo, Japan

³ Private Dental Practice, Hamedan, Iran

⁴ Dental Research Center, Mashhad University of Medical Sciences, Mashhad, Iran

Received 22 August 2019 and Accepted 4 November 2019

Abstract

The nickel-titanium (Ni-Ti) alloys used in endodontics contain 56% Ni and 44% Ti. The 2 unique features related to clinical dentistry (i.e., shape memory effect and superelasticity) are due to the transition from austenite to martensite in Ni-Ti alloy. When a superelastic Ni-Ti alloy undergoes a low tensile loading, normal elastic behavior occurs. In fact, at higher tensile loads, the elastic stress may reach a level at which there is extended horizontal region of elastic strain. The shape-memory property of Ni-Ti is derived from an atomic arrangement different from that of alloys like stainless steel. The purpose of this paper was to review the unique features of this alloy and mechanism of corrosion.

Keywords: Corrosion, Endodontics, Ni-Ti, Root Canal Preparation, Rotary Instrument

Mohammadi Z, Kinoshita J, Manabe A, Kobayashi M, Shalavi S, Jafarzadeh H. Corrosion of Ni-Ti Rotary Instruments: A Review. *J Dent Mater Tech* 2019; 8(4): 215-220.

Introduction

The nickel-titanium (Ni-Ti) alloys used in endodontic treatment contain 44% (wt) Ti and 56% (wt) Ni. In some alloys, small percentage of Ni may be substituted by the cobalt. This combination is a 1-to-1 atomic ratio of the major components, and similar to some other metallic systems. They have ability to alter their atomic bonding that may cause some unique changes in its important

mechanical properties. Temperature and stress can cause these kind of changes. The 2 unique features that are related to clinical dentistry (superelasticity and shape memory effect [SME]) may occur after a transition from austenite to martensite (1).

The concept of SME has been described by Ölander (2) during assessment of a cadmium-gold alloy. Beside SME, Ni-Ti exhibits superelastic behaviors that allow them to return to their original shape upon unloading following substantial deformation. Superelasticity may occur in correlation with reversible transformation between the austenite and martensite. Therefore, the transformation temperature and Ni-Ti behavior have an impact effect on its mechanical properties. This Ni-Ti property has induced a revolution in manufacturing the endodontic instruments with improved efficacy of root canal preparation (1).

When a superelastic Ni-Ti alloy undergoes low tensile loading, it shows normal elastic behavior. On the other hand, at higher tensile loads, the elastic stress may reach a level at which extended horizontal region of elastic strain may be observed. The elastic deformations in stainless steel (SS) and Ni-Ti are 3% and 7%, respectively. The SME of Ni-Ti is derived from an atomic arrangement that is different from alloys, such as SS. The atoms in SS can move against each other by a small specific amount before plastic deformation occurs (3).

Crystal characteristics of Ni-Ti alloy

All alloys with SME may show some changes in their atomic arrangement, characterizing some changes in the

phase while releasing or receiving the thermal energy. Deformation and shape recovery may be due to some changes in the lattice parameters during phase transformation between austenite and martensite (4). When Ni-Ti alloys are cooled through a transformation temperature, their inter-atomic bonding may be altered and so, its modulus of elasticity and yield strength may change as well. By decreasing the temperature, there are some changes in its crystal structure (martensitic transformation). The amount of this kind of transformation is a function of the martensite starts and finish temperature. The event causes some alterations in its physical properties and also allows the SME features (4).

Surface of Ni-Ti

The Ni-Ti surface consists of titanium oxides, small amounts of Ni oxides, and metallic Ni, while Ni-Ti constitutes the inner layer (5-10). The oxide layer thickness may vary from 2 to 20nm. Depending on the preparation technique, the surface chemistry and Ni amount may vary (11). The surface of untreated Ni-Ti is composed of carbon, oxygen, and titanium oxides with traces of Ni. The Ni oxide is not so stable so it may dissolve more easily than Ti. The surface of Ni-Ti arch wires has irregular features distinguished by island-like structures, where dissolution of Ni can occur (6).

Shabalovskaya (9) showed that by mechanical polishing of the surface, the Ti/Ni ratio was 5.5 (5 times more Ti on surface). When it was autoclaved, the Ni decreased and the Ti/Ni ratio increased. This was in agreement with Hanawa (5).

Pure Ti and some of its alloys are among the most biocompatible materials (11). The biocompatibility is due to the stable layer of Ti oxide. During implantation, the oxide layer grows and takes up minerals and some other constituents of bio-fluids, and these reactions may cause the surface remodeling. (5, 12, 13).

History of Corrosion

For the first time, Plato described corrosion as the product of iron and oxygen. These records described rust as the earth that is released from metal. In the 16th century, the Chemnitz city doctor, mayor, universal scholar and father of mineralogy, Georgius Agricola adopted this view in his large mineralogical work titled "Denatura fossilium". The term "corrosion" first appeared in a journal titled *Philosophical Transactions of the Royal Society*. At the end of the 18th century, the chemical nature of corrosion was identified. The physician and universal scholar Johann Wilhelm Ritter recognized the process of corrosion on metal in his theory in 1799 (14,15).

Definition

The term "corrosion" originates from the Latin verb *corrodere* and means to gnaw or eat away. According to this definition, it can be concluded that corrosion is a destructive or electrochemical reaction of a material with substances around it, which results in measurable changes in the material (16, 17).

Chemical Mechanism of Corrosion

If a Ni-Ti preparation instrument is immersed in an aqueous the sodium hypochlorite (NaOCl) solution (i.e., electrolyte solution), then the instrument (i.e., the electrode) acts as an electron conductor and the NaOCl solution (i.e., the electrolyte) as a medium in which the electrical current is transported through ions. The subsequent electrode reaction describes the phase boundary reaction equivalent to the charge exchange between the instrument and the NaOCl solution (4). The corrosion procedures take place on the phase boundary between the root canal instrument and the NaOCl solution; however, only negligible amounts of metal are converted.

The positively charged metal ions move to the anodic partial reaction in the electrolyte solution and leave the negatively charged electrons behind in the metal (i.e., the electron conductor), which means that the metal atom is oxidized. With the cathodic partial reaction, the dissolved metal ions at the phase boundary gather electrons and deposit themselves as metal atoms on the electrode surface. After the partial reactions, the flowing currents are termed as partial anodic current and partial cathodic current (18). In clinical terms, this phenomenon can also be seen through the blooming of a Ni-Ti instrument at the point of corrosion. It is also macroscopically visible that an external deposit has taken place (18, 19).

There is an electric potential form between the electrolyte and electrode, which makes it increasingly difficult for further ions to leave the metal until a balance is finally set. This balance is dynamic, as decomposition (i.e., anodic) and separation (i.e., cathodic) reactions are very large (5, 6). However, base and noble metals react differently if they are immersed in an electrolyte. The partial anodic current of the base metal, which is immersed in an electrolyte solution, is larger than the cathodic one as the base metal dissolves in the electrolytes. Electrons remain in the electrodes and consequently charge the electrodes negatively (20).

The metal ions dissolved in the electrolyte solution are positively charged and form a surplus, which charges the negatively-charged electrodes. With noble metals, the partial cathodic current is larger as these metals convert from dissolved to metal state. If the partial anodic or cathodic current prevails, an electrical double layer with a potential difference develops on the interface between

the electrode and electrolyte (2). However, this voltage between the electrode and electrolyte in a galvanic half-cell is not immediately measurable. The higher the quality of the metal, the less easy it is for the electrons to pass to the electrolyte solution and the higher the resting potential of the electrodes and vice versa.

If two galvanized half-cells of different metals are combined into one galvanized cell, a voltage source is formed. The voltage arises from a difference between the resting potentials and the positive pole of the noble metal. With this setup, the anodic dissolution predominates because the balance described above does not alter; however, corrosion occurs when the base metal continually disintegrates (18-20).

The Ni-Ti instruments are frequently used to treat root canals. These instruments are made up of 55% Ni and 45% Ti and contain light traces of iron and cobalt. The maximum period of use for a file depends on the strains and external influences that impact the instrument during the period of use. Corrosion, as a reaction of metals with their environment, is one of the numerous potential influencing factors. However, the corrosiveness does not just depend on the alloy composition, structure, and quality of the surface of the file (1, 18, 20). The frequency, type, and duration of the media that comes into contact with the instruments affect the passive layer of the instruments, which offers protection from corrosion.

In comparison with other alloys, the Ni-Ti alloy is characterized by its good resistance against corrosion. However, chloride ions, in particular, induce a corrosion process on Ni. Chloride ions are present in NaOCl irrigant that is frequently used in endodontic treatment (21). On contact with chloride ions, there is a risk of pitting corrosion, which are virtually unnoticeable without magnification. The frequency and duration with which a Ni-Ti file comes into contact with NaOCl solution influence the destruction of the passive Ti layer of the instruments (21).

Modification of the Ni-Ti surface

As far back as 1988, Walia et al. (22) claimed that the surface quality of Ni-Ti instruments needs considerable improvement. They recommended the electrolytic polishing of the surface of the instrument after treatment. While Lee et al. (23) suggested treating the instruments in a vacuum with nitrogen or boron to improve the surface quality and hardness and consequently reducing the wear of the instrument. An approximately 2 μ m ion-plated Ti-nitride layer or an approximately 2 μ m Ti-boron layer develops as a result of this treatment. These layers are believed to be particularly resistant to corrosion and particularly wear-resistant.

The cutting performance of the Ni-Ti instruments is improved as a result, and their service life is extended. It is possible to experimentally establish such ion-plated Ti-bromide layers on Ni-Ti instruments. These layers, in comparison with untreated Ni-Ti instruments, should double the hardness of the surface without affecting the flexibility of the alloy (23).

Rapisarda et al. (24, 25) were able to prove that the nitrating processes and nitrogen ion implantation can actually improve the cutting performance, decrease the treatment-related abrasion of the cutting edge, and increase the service life. Schafer et al. (26, 27) used a similar technology with physical vapor deposition coating to improve the cutting performance of Ni-Ti instruments. In this process, a 0.1 μ m adhesion-promoting layer made of Ti is formed to mechanically affect the properties of the Ni-Ti using a magnetically-filtered electric arc source with the temperatures of under 200°C in the vacuum. On this adhesive layer, a Ti-nitride layer with a thickness of about 1 μ m is then plated. Through this layer thickness, with a hardness of about 2200HV, the cutting edges experience clear wear protection and improvement of the cutting performance without the cutting edges being rounded by the additional layers (26, 27).

A recently introduced process is the cryo-treatment of Ni-Ti with -196°C liquid nitrogen. This treatment leads to a significantly greater micro-hardness in comparison with the untreated group (28). So far, the influences of these coatings and surface modifications on the corrosion of Ni-Ti have not been investigated in detail. With individual processes, it can only be assumed that a lower corrosion potential exists because of the higher surface quality.

Some metals, such as Ti, form a non-soluble solid coating spontaneously in the air or in neutral water. This coating is known as a passive layer. As a result, the metal and electrolyte are separated from each other, impeding and preventing the corrosion (6). In the literature, there is no standardized definition of the term passivity. On the one hand, it is recorded that the condition of passivity comes about through decreased corrosion speed (4). On the other hand, the high corrosion speed in combination with no or very low dissolution of metal is seen as the prerequisite for the development of a passive layer (29). The passive layer is a thin protective layer, with a thickness normally not higher than 1 to 10nm, which rests on the metal surface as a product of the reaction of the metal with the environment.

After the active dissolution of the metal, the formation of the passive layer normally follows in the form of oxides or non-soluble salts as a part of another anodic charge. The oxide layer prevents ions or water molecules from entering so that practically no more turnover of matter takes place (17). Therefore, the Ni-Ti

file has good inherent corrosion protection, which can protect it from corrosive attacks to a certain degree.

Corrosion of Ni-Ti Instruments

To inspect Ni-Ti for its susceptibility to corrosion, Ni-Ti alloys were subjected to a huge variety of tests. Edie et al. (30) rated the surface condition of Ni-Ti in comparison with SS, before and after clinical use, by means of a scanning electron microscope with a 100 to 1000 magnification. It became apparent that the surface condition of unused SS instruments was generally smoother than the unused Ni-Ti instruments. Upon visual inspection, no traces of corrosion could be observed on either SS or Ni-Ti. Even after the clinical use of the Ni-Ti instruments, no corrosion was evident.

However, an oxide layer develops on the surface of the Ni-Ti, which could be interpreted as corrosion itself, although this layer is visibly passive and leaves no obvious corrosion products (18). In a study by Rondelli and Vicentini (31), in order to simulate clinical conditions, commercially available Ni-Ti alloys were immersed in 40°C warm artificial saliva and physiological saline solution for comparison (0.9%). It was determined that Ni-Ti has sufficient resistance in the artificial saliva but it seems to be rather susceptible to corrosion in the physiological saline solution (19). The 11-month storage in 1% saline solution caused corrosion on the surface of the Ni-Ti alloys but did not affect the flexibility (32).

In particular, the contact of Ni-Ti instruments with NaOCl has various results. Aten et al. (33) were able to determine the traces of corrosion through separation. Within 1-12 h, it was clearly macroscopically visible on Ni-Ti instruments after the contact with 5.25% NaOCl solution and in combination with five treatment cycles and subsequent sterilization. Busslinger et al. (34) used 1% and 5% NaOCl solutions placed in plastic bottles in an ultrasonic bath while they came into contact with the Ni-Ti instruments. With a 1% concentration of the NaOCl solution, no corrosion could be seen even after an exposure time of 60 min. On the other hand, the visible traces of corrosion occurred after the immersion of the Ni-Ti instruments in the 5% NaOCl solution at an exposure time of 30 min. Darabara et al. (35) heated the 5.25% sodium hypochlorite solution so that the liquid maintained a constant temperature of 37°C during the test. The result was a high corrosion resistance of Ni-Ti in the NaOCl solution.

O'Hoy et al. (36) carried out cleaning cycles on the Ni-Ti files with both 1% NaOCl solution and Milton solution, a mixture of 1% NaOCl solution and 19% NaCl solution and were able to show that no corrosion occurred. However, if the files were left overnight (i.e., 18 h) without additional influence on the liquids, the

traces of corrosion through separation were visible. In 1997 and 1999, Stokes et al. (37, 38) carried out similar tests. They immersed Ni-Ti files in a 5.25% NaOCl solution and then examined for corrosion. The findings were inconsistent as some files corroded but others did not. In electrochemical polarization tests, significant corrosion of Ni-Ti upon contact with NaOCl occurred with the voltages of -0.6 to 1.0V using an atom absorption spectroscope and energy dispersive X-ray analysis (39).

References

1. Thompson SA. An overview of nickel-titanium alloys used in dentistry. *Int Endod J.* 2000; 33(4):297-310.
2. Ölander A. An electrochemical investigation of solid cadmium gold alloys. *J Am Chem Soc* 1932; 54(9):3819-3833.
3. Mohammadi Z, Soltani MK, Shalavi S, Asgary S. A Review of the Various Surface Treatments of NiTi Instruments. *Iran Endod J.* 2014; 9(4):235-240.
4. Otsuka K, Ren X. Physical metallurgy of Ti-Ni-based shape memory alloys. *Progress Med Sci.* 2005; 50:511-678.
5. Hanawa T, Hiromoto S, Asami K, Okuno O, Asaoka K. Surface oxide films on titanium alloys regenerated in Hanks' solution. *Mater Transact.* 2002; 43(12):3000-3004.
6. Endo K. Chemical modification of metallic implant surfaces with biofunctional proteins (Part 1). Molecular structure and biological activity of a modified NiTi alloy surface. *Dent Mater J.* 1995; 14(2):185-198.
7. Endo K. Chemical modification of metallic implant surfaces with biofunctional proteins (Part 2). Corrosion resistance of a chemically modified NiTi alloy. *Dent Mater J* 1995; 14(2):199-210.
8. Oshida Y, Sachdeva RC, Miyazaki S. Microanalytical characterization and surface modification of Ti-Ni orthodontic archwires. *Biomed Mater Eng.* 1992; 2(1):51-69.
9. Shabalovskaya SA. On the nature of the biocompatibility and on medical applications of NiTi shape memory and superelastic alloys. *Biomed Mater Eng.* 1996; 6(4):267-289.
10. Yahia LH, Ryhänen J. Bioperformance of shape memory alloys. *Shape Memory Implants.* New York: Springer, 2000.
11. Vadiraj A, Kamaraj M. Effect of surface treatments on fretting fatigue damage of biomedical titanium alloys. *Tribol Int.* 2007; 40(2):82-88.
12. Hanawa T, Ota M. Calcium phosphate naturally formed on titanium in electrolyte solution. *Biomaterials.* 1991; 12(8):767-774.

13. Hanawa T, Asami K, Asaoka K. Repassivation of titanium and surface oxide film regenerated in simulated bioliquid. *J Biomed Mater Res.* 1998; 40(4):530-538.
14. <https://en.wikipedia.org/wiki/Corrosion>
15. Tostmann KH. *Korrosion–Ursachen und Vermeidung.* Berlin: Wiley-VCH, 2000.
16. Gellings PJ. *Korrosion und Korrosionsschutz von Metallen.* Hanser, Munchen, 1981:123-5.
17. Marxkors R, Meiners H. *Taschenbuch der zahnärztlichen Werkstoffkunde.* Hanser, Munchen, 1993:42-7.
18. Yahia L, Manceur A, Chaffraix P. Bioperformance of shape memory alloy single crystals. *Biomed Mater Eng.* 2006;16(2):101-108
19. Hasegawa Y, Goto S, Ogura H. Effect of EDTA solution on corrosion fatigue of Ni-Ti files with different shapes. *Dent Mater J.* 2014;33(3):415-421
20. Gill P, Musaramthota V, Munroe N, et al. Surface modification of Ni-Ti alloys for stent application after magnetoelectropolishing. *Mater SciEng C Mater Biol Appl* 2015; 50:37-44.
21. Mohammadi Z. Sodium hypochlorite in endodontics: an update review. *Int Dent J.* 2008; 58(6):329-341.
22. Walia H, Brantley WA, Gerstein H. An initial investigation of the bending and torsional properties of nitinol root canal files. *J Endod.* 1988; 14(7):346–351.
23. Lee TH, Huang TK, Lin SY, Chen LK, Chou MY, Huang HH. Corrosion resistance of different nickel-titanium archwires in acidic fluoride-containing artificial saliva. *Angle Orthod.* 2010; 80(3):547-553.
24. Rapisarda E, Bonaccorso A, Tripi TR, Fragalk I, Condorelli GG. The effect of surface treatments of nickel-titanium files on wear and cutting efficiency. *Oral Surg Oral Med Oral Pathol Oral Radiol Endod.* 2000; 89(3):363-8.
25. Rapisarda E, Bonaccorso A, Tripi TR, Condorelli GG, Torrisi L. Wear of nickel-titanium endodontic instruments evaluated by scanning electron microscopy: effect of ion implantation. *J Endod.* 2001; 27(9):588-592.
26. Schafer E. Effect of physical vapor deposition on cutting efficiency of nickel-titanium files. *J Endod.* 2002; 28(12):800-802.
27. Schafer E. *Metallurgie und Eigenschaften von Nickel-Titan-Instrumenten.* In: Hulsmann M: *Wurzelkanalaufbereitung mit Nickel-Titan-Instrumenten.* Berlin: Quintessenz, 2002.
28. Kim JW, Griggs JA, Regan JD, Ellis RA, Cai Z. Effect of cryogenic treatment on nickel-titanium endodontic instruments. *Int Endod J.* 2005; 38(6):364-371.
29. Oetken M, Rottgen C, Jansen W. Die Passivität der Metalle. *Praxis der Naturwissenschaften – Chemie.* 1996; 45(1):15-20.
30. Edie JW, Andreasen GF, Zaytoun MP. Surface corrosion of nitinol and stainless steel under clinical conditions. *Angle Orthod.* 1981; 51(4):319-324.
31. Rondelli G, Vicentini B. Localized corrosion behaviour in simulated human body fluids of commercial NiTi orthodontic wires. *Biomaterials.* 1999; 20(8):785-792.
32. Schwaninger B, Sakar NK, Foster BE. Effect of long-term immersion corrosion on the flexural properties of nitinol. *Am J Orthod.* 1982; 82(1):45-49.
33. Aten JC, Osetek EM, Heuer MA, Lautenschlager EP. The simulation of clinical corrosion of endodontic files. *Northwest Dent Res.* 1994; 5(1):3-4.
34. Busslinger A, Sener B, Barbakow F. Effects of sodium hypochlorite on nickel-titanium Lightspeed instruments. *Int Endod J.* 1998; 31(4):290-294.
35. Darabara M, Bourithis L, Zinelis S, Papadimitriou GD. Susceptibility to localized corrosion of stainless steel and NiTi endodontic instruments in irrigating solutions. *Int Endod J* 2004; 37(10):705-710.
36. O'Hoy P, Messer H, Palamara J. The effect of cleaning procedures on the fracture properties and the corrosion of NiTi files. *Int Endod J.* 2003; 36(11):724-732.
37. Stokes OW, di Fiore PM, Barrs JT, Gilbert JL, Lautenschlager EP. Corrosion in stainless steel and nickel titanium files (Abstr. Nr. OR 7). *J Endod.* 1997; 23(6):251.
38. Stokes OW, di Fiore PM, Barrs JT, Koerber A, Gilbert JL, Lautenschlager EP. Corrosion in stainless-steel and nickel-titanium files. *J Endod.* 1999; 25(1):17-20.
39. Kuphaksuk C, Oshida Y, Andres CJ, Hovijitra ST, Barco MT, Brown DT. Electrochemical corrosion of titanium and titanium-based alloys. *J Prosthet Dent.* 2001; 85(2):195-202.

Corresponding Author:

Hamid Jafarzadeh

Dental Research Center

Vakilabad Blvd, Mashhad, Iran

P.O. Box: 91735-984

Tel: +98-51-38829501

Fax: +98-51-38829500

E-mail: hamid_j365@yahoo.com & JafarzadehBH@mums.ac.ir