CORROSION CHANGES OF WELDABLE NITINOLS (NiTi) IN AN ENVIRONMENT OD PHYSIOLOGICAL LIQUIDS

Katarzyna KAPUSTKA[a], Maciej HAJDUGA[a], Dariusz JĘDRZEJCZYK[a], Joanna WAŚ-SOLIPIWO[b]

[a] *University of Bielsko-Biala, Bielsko-Biala, Poland, EU*
[b] *BOSMAL Automotive Research and Development Institute, Bielsko-Biala, Poland, EU,*
katarzynakapustka@op.pl

Abstract

From the large number of available metals with the memory of shape only a few of them found clinical application. Biocompatible orthodontic wires, applied in case of false occlusion reconstruction, are made of intelligent materials and components. The phenomenon origins from the material's property called "shape memory". The alloy deformed plastically in the lower temperature regains its initial shape in the higher temperature. Orthodontic wires, due to their purpose and use, succumb to damage. Hence the exploitation in very demanding conditions of oral cavity makes us search for very efficient reparation system. From the large number available materials with a shape memory only few of them complied with clinical application. It is a result of tough criteria measures implemented to implants - targeting fulfilling biological requirements. Austenitic steels, applied in medicine, belong to metallic biomaterials particularly exposed to damage, due to ongoing processes of corrosion strain. It is connected with its weakest resistance to electrochemical corrosion in environment of organism fluids hence lower susceptibility to self-passivation. The appearance of the foreign matter in the organism stimulates many mechanisms aiming its elimination. So if the foreign substance, in this case the wire, is traced by immunological system, the organism starts production of anti-bodies of strong oxidizing functions. Antibodies consolidate near the implant and absorb into biomaterial. Defensive reaction of the organism is becoming one of the reasons of degradation of biomaterials. The work is devoted to the influence of corrosion environment on the structure and properties stability of NiTi wires after reparation.

Keywords: Corrosion, nitinol, argon envelope, soldering, heat sealing

1. INTRODUCTION

According to Vermilyea corrosion of metals is a craft rather than a science. At the moment we have too small fund of knowledge to our disposal to be able to predict with sufficient certainty how a particular metal or alloy will behave in a particular environment. Decisions on the selection of a suitable metal tend to be based more on the results of previous experiments and trials than on a scientific basis. "In the field of corrosion knowledge, technology significantly advances the theory" [1]. Intelligent material does not have a universally accepted definition. It is most often defined as a material which is able to respond to external stimuli by a significant change of its properties for the desired effect. A shape memory effect is based on martensitic transformation. Martensitic transformation is a transformation of the first kind, so occurs through the nucleation and growth of a new phase nucleus. Its main feature is non-diffusive nature of displacement. The term "non-diffusive" means that it does not require diffusion of atoms over long distances, so it does not occur during the migration through the separated boundaries and martensite parent phase [2,3] .

Shape memory alloys are a unique class of metal alloys. Among these materials, more than 90 % of commercial applications have NiTi based alloys, showing also the best mechanical properties.

Biocompatible orthodontic wires applied to reconstruct defective occlusion are made of smart materials. A significant advantage of NiTi wires in comparison with steel wires is six-fold lower modulus of elasticity, so it means that for the same deflection for NiTi wire much smaller forces are obtained. From a clinical perspective it is clear that the nitinol wire exerts less pressure on the bite force of a steel wire. Orthodontic arches due to its destiny are subject to frequent damage. Working in the demanding conditions of the oral cavity they need effective way of repair [4]. The emergence of foreign body in a living organism stimulates a lot of mechanisms to remove it. When a foreign substance, in this case a wire, is detected by the immune system, the body begins to produce antibodies with a strong oxidizing agent. Antibodies accumulate in and around the implant to absorb the biomaterial. Defensive reaction of the organism becomes one of the causes of degradation of biomaterials [5]. Constantly used metallic biomaterials are particularly vulnerable to destruction as a result of stress corrosion processes. It is associated with the lower resistance to the electrochemical corrosion in environment of the body fluids and a lower tendency to self-passivation [6].

The work's purpose was to find the proper way of NiTi wires repair, which for various reasons have been damaged and deformed. With reference to the application, they are also often destroyed and repair costs normally are covered by the patient. The present literature does not convey up too much information about the repaired elements made of a shape memory material. Currently, there are a lot of different methods of connecting metallic materials, and the problem arises from not how to connect but which method should be chosen. During the Bronze Age man chose between belting and impaction, today's engineer may find four or five different ways, equally useful.

The paper presents the environmental impact of corrosion on the effectiveness of the NiTi wires self-repairing. The simultaneous interaction of the corrosive agent and the tensile and compressive stress causes the resistance of the metal structure decreases. You should expect faster accelerate on of the destruction of steel used for heavy loads, among others, in orthodontics, maxillofacial surgery, orthopedics and traumatology.

2. OWN INVESTIGATIONS

2.1 Aim of the study

The aim of the study was to assess the correctness of the various ways repair process of orthodontic wires. As well as the quality assessment of a joint of two orthodontic wires, which for various reasons have been damaged. Next the construction of combinations of the aforementioned structural metallic materials bonded (connected) by methods such as welding (argon Dent method PUK), welding, and brazing (using solder CoCrMo). The influence of corrosive environment on the effectiveness of the NiTi wires repairing ability. As well as to determine the impact of corrosion on the continuity of the nitinol-nitinol connection.

2.2 Scope of work

The scope of work includes metallographic macroscopic and microscopic connection structures analysis. NiTi material of different chemical composition of two manufacturers: Rematitan - Dentaurum and Ortho Organizers - Nitanium was used. The predominant structural elements of this alloy is Ni and Ti in suitable proportions percentages of ingredients. During investigations also hardness tests of the base metal and weld in the place of repair were performed. Based on these studies we can try to evaluate the strength of the joints Rm - static tensile test. The samples were subjected to the corrosion test. Electrochemical measurements of DC to assess the corrosion resistance. They consist in recording the polarization curves in a conventional three-electrode system according to DIN EN ISO 10271. Physiological corrosive environments was achieved by the use of artificial saliva, Ringer's solution, artificial blood [7]. The conducted tests regarded NiTi material produced by: Ortho Organizers - Nitanium, with a constant chemical composition.

2.3 Materials tests

During the materials tests the orthodontic wires, i.e., nickel-titanium alloys were used. Chemical composition of applied wires: Rematitan - Dentaurum ®, and Nitanium - Ortho Organizers ® is enclosed in **Table 1**. An example of damaged rectangular wires (0.48 mm × 0.65 mm) is shown in **Fig. 2a**. The gauge length of a test piece in tensile test was L_0 = 150 mm. Samples for hardness determination were hot mounted in test specimen (**Fig. 2b**) with 35 mm diameter. Corrosion resistance was determined in the bonding areas, and the heat affected zones lengthwise of 0.5 mm (**Fig. 2c**). The surfaces have been properly prepared in accordance with the standards (BS EN 1321 2000 PN-84/H-04507.01, BS EN 1002-1:2004, BS EN ISO 10271) for individual research.

Table 1 Chemical composition of applied wires

Kind of wire	**Chemical composition, %**			
	According standard		According chemical analysis	
	Ti	Ni	Ti	Ni
Rematitan	Rest	50-60	43,7	56,3
Nitanium	43,7	56,3	43,9	56,1

To evaluate the chemical composition of the wire an X-ray microanalyzer Oxford ISIS 300 was used. Values according chemical analysis are within the limits given by the producer (**Table 1**). Despite the similar chemical composition of NiTi wires being compared, they exhibit different corrosion properties (according to Huang). For the study 15 samples for each connection were prepared. In total, 100 samples were tested [8].


a) b) c)

Fig.1 The appearance of tested samples: a) damaged orthodontic arch, b) hot mounted samples of repaired NiTi, c) sample for corrosion test

2.4 Applied repairing - welding

Tested orthodontic Ni-Ti wires were jointed using the welder type DentaPuk. The length covered by the weld arc was 5 mm. Welding treatment was performed under argon to avoid the drawbacks caused when the tip in contact with the workpiece electrode closes an electrical circuit and automatically starts the welding process. Arc light "pulls" the starting point of contact. Welding point with a diameter of 0.4 mm results in melting of the metal and formation of stable connection area. Through the angle at which the electrode touches the workpiece exerted energy flows during welding. In this way you can control the welding in the desired direction-as.

2.5 Soldering

To soldering orthodontic wire gun solder of CoCrMo alloys was applied, where the range of temperature between 1100-1200 °C can be reached. The energy required to melt the solder is generated by manual gas burner. The problem is the temperature control - too high or too low temperature might lead to overheating of the whole structure, creation of inaccurate melt solder and carburization of the connection. Applied temperature range can cause further changes in surface and structure. Joining mechanism has a diffusive character and results in a very tough structure.

2.6 Heat sealing

To connect the test material by heat-sealing, SU-Dentafix device has been used, applying the following parameters: current equal to 4A, the holding time of the welding electrodes - 0.4 s. This is a classic counter sealer used in dental laboratories. The device is simple to use and the process of combining is relatively short. The applied method was based on a local welding of thermal plasticized NiTi pieces, then their pressure.

3. RESULT'S DISCUSSION AND CONCLUSIONS

3.1 Macroscopic observations

To observe selected - the most characteristic macroscopic samples of NiTi wires connected by different methods a stereoscopic microscope at a magnification of 20 times was used. The typical results are given in **Fig. 2**. The welded joints demonstrate relatively good structural homogeneity. Lack of visible discontinuities suggests a high quality connection. A small area of heat affected zone is an advantage of this method. All the connections passed the macroscopic examination as the initial control level and no major surface structural defects were detected. In the solder connection the weld discontinuities and lack of adhesion to the joined surface can be observed. This may be the result of surface tensions of solder fillings, resulting in the occurrence of internal stresses, resulting in the destruction of the connection areas. In the heat sealing connection a uneven distribution of the points of application of the electrode is visible. This has an impact on possibility of different external loads transfer, and thus the mechanical deformations.

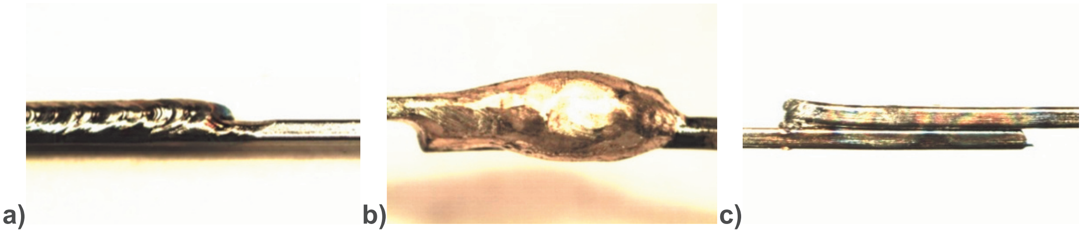


Fig.2 Macroscopic examination magnif.20×, a) welding in argon envelope, b) soldering, c) heat sealing

3.2 Microscopic studies

Optical microscopy was applied to assess the micro - structure of welded, brazed and heat-sealed NiTi wires and their continuity. Micro-sections were prepared according to the standard, then the samples were etched to reveal the microstructure especially in created connection. Microstructure observed under optical microscope NEOPHOT 2, at a magnification of ×100, and ×500, is presented in **Fig. 3-5**.

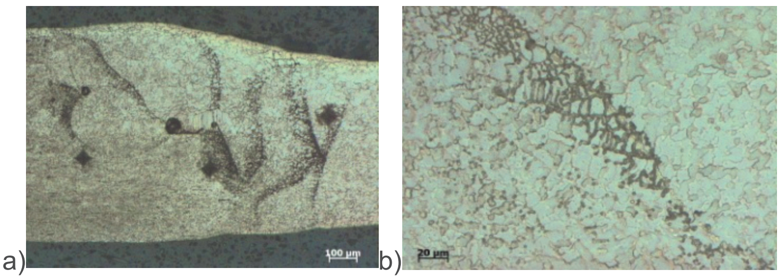


Fig.3 The structure of the NiTi connection welded in argon envelope, etched a) mag. 100×, b) mag. 500×

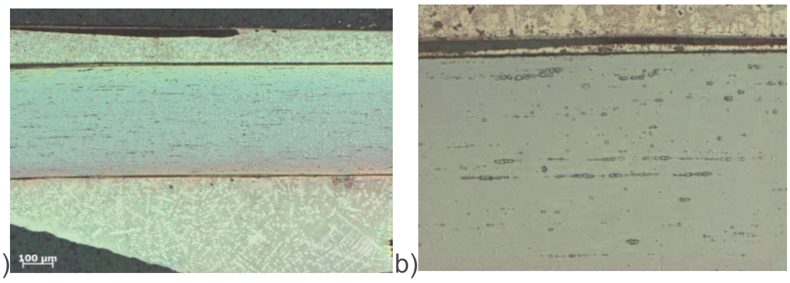


Fig.4 The structure of NiTi soldering connection, etched a)mag. 100×, b) mag. 500×

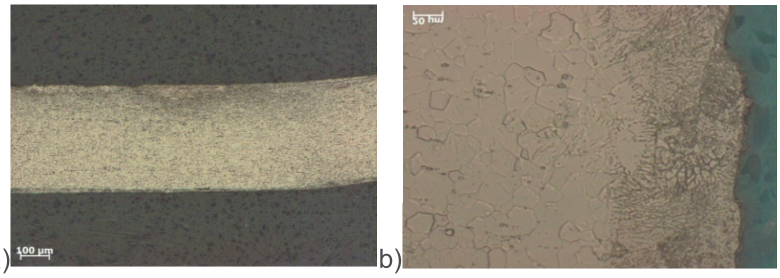


Fig.5 The structure of heat sealed NiTi connection, etched a) mag. 100×, b) mag.500×

Microscopic examination of welded area cross section at a magnification of × 100 (**Fig. 3**) revealed the darker places - less resistant to corrosion (to used etching reagents) being probably the result of zonal segregations caused by variable solubility of alloy’s impurities, that can affect essentially also the measured Rm values. The more precise conclusions can be formulated after additional RTG analysis. **Fig. 4b** presents the observed structure at magnification 500 × - the structure is not homogenous and is composed of a various areas with regular grains and also inter-dendritic precipitations. **Fig. 5**a shows the structure of NiTi wire connection created by soldering. The structure is homogeneous and the filler penetration is satisfactory - there is no porosity on joined surfaces. There is no great influence of temperature on micro-structures changes. Both connected surfaces and the sub-surface structure do not reveal any impurities. Solder has a typical dendritic structure, without any diffusive process influence (too low temperature). Because of too low connection strength this type of joining does not meet expectations. The use of high temperatures in the case of heat sealed joining results in the needle structure observed in subsurface layer. Structure change visible in details in **Fig. 9**b are not the result of deliberate action. However, probably the better selection of the process parameters will allow to obtain a more satisfactory connection properties.

3.3 Tensile strength measurement

On the basis of measured tensile strength values we can conclude that the most satisfactory result were achieved in the case of welding in argon atmosphere and soldering. On the other hand the highest hardness value was measured in heat sealed connection. It can be caused by high temperature influence and formation of needle structure.

3.4 Corrosion in physiological fluids

The kind of Ni-Ti wires joining affect the measured and set parameters of electrochemical corrosion process (10 - minute exposure in the artificial saliva solution, Ringer's solution and artificial blood). Conditions during the test were as follows: temperature of 36,6-37 ° C and pH = 7,6 for artificial Ringer KWRI and pH = 8,7 and the artificial saliva. A method of wires repair affects the value of the anodic current, the potential of the anodic-cathodic transition (CE -A) and the nucleation potential. The highest growth of potential of pitting nucleation (EW) was found for soldered wire, while the smallest values were measured for wire welded in atmosphere of argon. The corrosion rate was determined for every applied joining method in the individual occurring physiological fluids.

Table 2 The relation between corrosion rate, reparation method and corroding medium

Reparation method	Corrosion rate [mm/year]	Polarization resistance [kΩ]	Corrosion rate [mm/year]	Polarization resistance [kΩ]	Corrosion rate [mm/year]	Polarization resistance [kΩ]
	ARTIFICIAL SALIVA SOLUTION		RINGER'S SOLUTION		ARTIFICAL BLOOD	
WELDING	0,0003	779,5	0,043	61,4	0,0166	50,5
SOLDERING	0,0626	1,7	-	-	0,0073	6,1
HEAT SEALING	0,0006	347,7	0,0019	308,6	0,0024	151,7
ELEMENTARY MATERIAL	-	-	0,0238	2,9	0,25	2,99

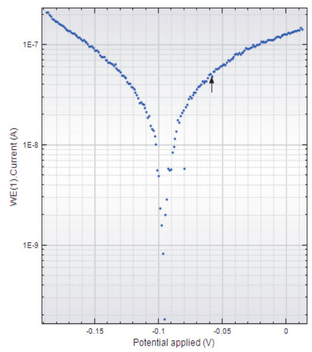
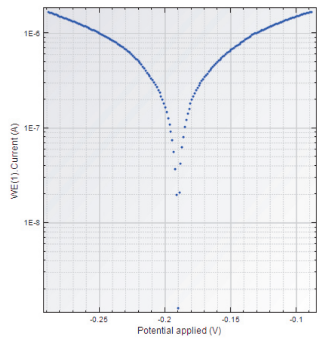
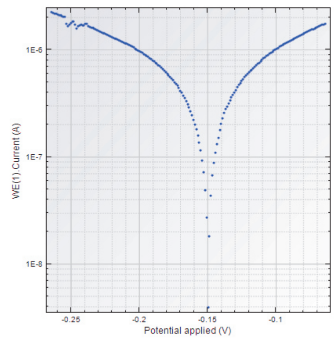
ARTIFICIAL SALIVA SOLUTION	RINGER'S SOLUTION	ARTIFICIAL BLOOD
		

Fig. 6 Linear polarization in various corroding medium

Conducted tests revealed interesting relationship (in corrosion terms) between the joint type and the kind of corroding medium. Some of the parameters values presented in **Table 2** are lower for elementary material than for created joints. Polarization resistance parameter express the nature of the body fluids action. The highest values were measured for heat-sealing joint in an artificial blood and Ringer's solution whereas in the artificial saliva solution the welded joint in argon envelope demonstrated the highest polarization resistance value. Achieved results indicate that in these cases/ connections aggressiveness of the environment is reduced and calculated corrosion rate is much more lower. The stationary potential characterizes the nobility of the surface of repaired place. The higher potential values were measured for the welded joint inside the artificial blood and artificial saliva. However in Ringer's solution the best parameters values were measured for heat sealing joint. It follows from conducted experiment that, the selection of proper connection method should be based on both strength parameters and corrosion resistance. In order to ensure the highest protection against the corrosion (leading to metallosis inside the soft tissues of the body) not only the construction loading should be considered but above all the influence of environment where the construction will be applied.

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