

# STRESS CORROSION CRACKING OF MODIFIED NITI ALLOYS IN CHLORIDE SOLUTIONS

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## Abstract

Shape memory and superelastic alloys are commonly used in biomedical and engineering areas, due to their higher elastic deformation characteristics and low elastic module when in martensitic state. For these applications, it is necessary that the alloy exhibit adequate corrosion resistance, especially in chloride environments, being biocompatible for biomedical applications. The addition of ternary elements to the NiTi alloy aim the adjust of mechanical properties and can affect the corrosion resistance. Additions of elements such as Co increase the elastic limit and reduce the transformation temperature; Cr additions increase the yield strength of the alloys together with stiffness and fatigue resistance. This study aim to evaluate the behavior of NiTi alloys with Co and Cr additions, compared to binary alloys under stress in NaCl 0.9% medium. Mechanical tests were performed to determine the superelastic response of each alloy, followed by potentiodynamic and potentiostatic electrochemical tests. The potentiostatic tests evaluated the correlation between anodic current and deformation of the material. It was concluded that, despite the mechanical benefits provided by the addition of ternary elements, these additions can increase the susceptibility to stress corrosion cracking of the ternary alloys in a chloride environment.

Keywords “corrosion”, “shape memory alloys”, “NaCl”, “biomaterial”, “orthodontic wires”

## **Introduction**

NiTi alloys exhibit shape memory and superelasticity properties and are referred to as Shape Memory Alloys (SMA). This behavior allows the biomedical use as special devices in orthopedics, cardiology, neurology and orthodontics applications. More recently, this material is being employed in oil and gas industry as packers, actuators, blowout, connections, couplers and fasteners [1].

The choice of this alloy is based on their elastic deformation capacity due to the crystallographic reversible transitions from cubic austenitic phase B2 to monoclinic martensitic phase B19' [1]. The mechanical properties of NiTi alloys can be adjusted and improved by the additions of ternary and quaternary elements. This addition may change properties by changing the critical transformation temperatures, decreasing the mechanical hysteresis, improving the superelasticity plateau and inducing radiopacity [2,3]. However, together with these mentioned modifications, the corrosion resistance can be affected.

Addition of Co increases the yield stress and decreases the  $M_s$  critical temperature transformation, within 1 to 2 % addition [4,5]. The addition of 1 % Cr can be sufficient to improve the fatigue resistance and elastic modulus. The same Cr addition decreases  $M_s$  and  $A_s$  critical temperature transformation [6-8].

The addition of third and quaternary elements to the alloy can change the passive film composition and passive film growth kinetics. The surface treatment of the alloy can affect the nature of the oxide film formed as presented in literature [9-15]. Literature claims that use of surface treatment in binary and ternary alloys has no influence on the comparative corrosion resistance of the alloys. Several authors [4, 7, 9, 11, 15] evaluated the corrosion resistance of binary and ternary alloys, such as NiTiPd, NiTiFe and NiTiCu, without surface treatment in NaCl 0.9% solution. The authors observed a difference of corrosion resistance between the ternary and binary alloys based on the obtained electrochemical parameters. The binary alloys showed a higher corrosion resistance than the ternary alloys and this result was associated to the composition of the passive film formed on the surface of each alloy.

Besides that, in biomedical applications as orthodontic wires and vascular stents, the devices can work under stress in the presence of the corrosive body fluid. The pseudoelasticity of these alloys permits the application of low forces necessary to promote the teeth movement in orthodontic applications and allows the stents to support the lumen of blood vessels under compression during systolic contraction. Considering the use under stress and strain in several NiTi applications, assessment of the corrosion resistance on this condition is relevant [3,4,6,7,11,14-19].

Crystalline structure under stress and the composition of the alloy can influence the corrosion resistance [20-22, 25, 26]. However, RONDELLI & VICENTINI [24] observed no changes on the corrosion resistance of binary alloy under 4% load stress. This condition corresponds to the superelastic transformation of austenite to martensite. The corrosion parameters obtained by the authors suggest that the resistance of the passive film under load and the presence of martensitic phase do not change the corrosion resistance. WANG et al [21] observed no significant difference of pitting potential values between under stress and without stress NiTi wires. However, the authors explained that the elastic deformation may break the passive film, directly exposing the surface to the corrosive environment in the film rupture region, where active dissolution can occur. When, the stress is constant, the film can repassivate. Despite the changes in the corrosion, parameters are not significant under load, the material can undergo changes in its surface. Therefore, the material may be in cyclic disruption - repassivation process, which leads to cracking under stress corrosion.

Since the NiTi alloys in various applications are subject to stress and strain, this work proposed to evaluate the influence of strain on the passive state of NiTi and modified NiTi alloys in NaCl 0.9% solution through amperometric tests.

## Materials and Methods

Preliminary mechanical tensile tests were performed in air in order to determine the superelastic plateau of each alloy. From stress and strain plateau values, the electrochemical and mechanical tests were performed in corrosive environment. The materials were evaluated at constant and variable strain in the plateau corresponding to the presence of two crystallographic phases - austenite and martensitic.

### Materials

The binary alloy used were the NiTi0.024 in. wire fabricated by Memory-Metalle GmbH, Germany. The ternary alloys used were the NiTiCo 0.018 in. and NiTiCr 0.019 in. wires fabricated by Memry Corp, Bethel, Connecticut, USA. The body simulated solution used were NaCl 0.9 % according to ISO 10993-15.

### Mechanical tests in air

The mechanical tests in air were performed using a Hounsfield Tensometer - series n° 8749 linked to a load cell Alfa Instrument 3102, displacement transducer Mutoyo attached to the computer (Figure 1). The wires were tested with working length of 130 mm and a pre-loaded up to 3.0 kgF using a slow and constant strain rate equal to  $1.5 \times 10^{-3}$  mm/s, until achieve the plastic deformation plateau.



*Figure 1 - Horizontal tensile used for the mechanical tests, working length wire of 130mm.*

### Electrochemical tests

The electrochemical measurements were performed using three electrode configuration cell and potentiostat ( $\mu$ Autolab Type III) according to the ASTM G5. Before the potentiostatic measurements, potentiodynamic anodic polarization under constant load were performed in order to obtain the passive range of each alloy in the solution. The stress and strain applied corresponds 50% of deformation on superelastic plateau for each alloy tested. The value of load applied were based in the results obtained from the mechanical tests in air.

The amperometric measurements were made in three steps. The duration of each step was 7200s. The purpose of these steps was to evaluate the capacity of the passive film to follow the elastic deformation of the material and the repassivation ability when the film was broken. The electrochemical parameter registered in all three steps were the anodic current versus time at a constant potential.

The first step carried out in order to evaluate the behavior the passive film under constant strain corresponding to the pseudoelastic plateaus of the stress-strain curve. The duration of this step

was fixed in 7200 seconds, as mentioned, or a cutoff anodic current equal to  $10^{-2}$  A, whichever comes first.

The second step was designed to evaluate the passive film behavior under continuous straining up to 7200 s with low speed equal to  $1.5 \times 10^{-3}$  mm /s, the same used in mechanical tests in the air.

The third step was carried out to evaluate the film passive film behavior when the strain stopped or, in other words, to assess the repassivation ability of the passive film.

During all steps, the material remained within the pseudoelastic regime as show in Figure 2. The straining wires were used as working electrodes and anodic current time profiles were obtained by the potentiostat attached to the electrochemical cell designed to perform the experiments. This cell contains 3 electrodes: saturated calomel as reference electrode, platinum wire as counter electrode and the wire of each alloy as working electrode.

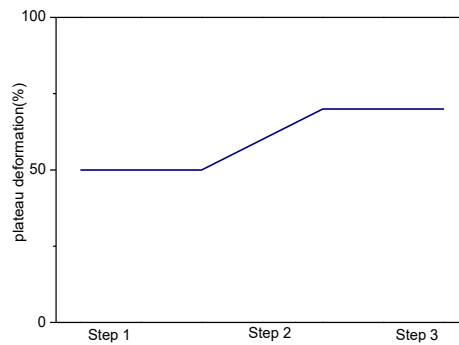


Figure 2 – Representation of the straining steps imposed.

## **Results and Discussion**

### Mechanical preliminary tests

The superelastic plateau data of the alloys with respective values of stress and elongation limits are indicated on Table 1. Condition adopted to perform step 1 test is indicated on the same table as Test Strain.

Table 1- Means stress values and % strain limits of superelastic plateau

Alloy	Superelastic plateau means	Start plateau	Final plateau	Test strain
NiTi	400 MPa	0.58%	5.8%	3%
NiTiCo	703.8 MPa	1.4	6.8%	4.1%
NiTiCr	467.8 MPa	0.6%	7.96%	4.35%

It is evident that the addition of the ternary elements changes the mechanical properties of the material. The addition of Co increases the pseudoelastic plateau stress values for the mean value of 703.8 MPa, which is consistent with the results presented by FASCHING et al. [4]. These authors obtained 710 MPa for the pseudoelastic plateau of the same alloy.

The addition of Cr did not significantly alter in the average stress values of plateau when compared to the binary alloy, as cited by ZARINEJAD & LIU [2], which affirmed that the main purpose of adding Cr to the alloy would be to decrease the critical temperatures phase transformation, making it more close to ambient temperature. FROSTCHER et al. [8] obtained

a plateau equal to 500 MPa for NiTiCr wires with 0.25% Cr, the same composition used in this work where the value obtained was 467.8 MPa. Straining limits were very similar. The authors obtained from 0.85 and 6% of elastic deformation within the plateau limits, similar to the limits obtained in the present work, within 0.6 and 7.9%.

The binary alloy NiTi presented 0.6% strain at the beginning and 5.8% at the end of the plateau, confirming the data reported by HENDERSON et al. [22], 1% to 6%. SHABALOVSKAYA et al. [23] also reported the elastic deformation values, with values close to 5.5% at the end of plateau. The value of elastic deformation initial cited by RONDELLI & VICINETINI [24] for the binary alloy were 1%, nearly to the value obtained in this work. The stress values of superelastic plateau here obtained, 400 MPa, were close to data obtained by KASSAB et al. [25], from 392.65 MPa to 400.3 MPa for the binary NiTi alloy.

### Electrochemical tests

Preliminary electrochemical tests on the unstressed materials were carried out to determine the anodic potential to be used on steps 1, 2 and 3. The results are shown on Table 2, corresponding to an anodic potential in the middle of the passive range of each alloy, corresponding to the median potential value of the passive range. The constant potential values were used for the amperometric tests on the tensile test

*Table 2 - Median anodic potential in the passive range of each alloy applied in amperometric tests.*

Alloy	Applied Potential (SCE)
NiTi	390mV
NiTiCo	206mV
NiTiCr	270mV

### Step 1

The amperometric response, which means the anodic current versus time, was obtained with the application of a constant anodic potential as shown on Table 2. The material was stressed during 7200 s. The initial and final deformation were in the elastic deformation regime for all specimens tested for each alloy in all the next steps. The binary alloy presented stable passive current during the test, and consequently a stable passive film with the ability to remain stable under pseudoelastic constant strain. Incidence of localized corrosion did not occur with the strain induced phase transformation of the alloy.

The ternary alloys, with additions of Co or Cr presented stable behavior of passive current during the test, for 2 out of 3 specimens tested. The third specimen of each ternary alloy presented an increase of the anodic current due to the rupture of the passive film with the occurrence of localized corrosion under constant strain. The behavior of ternary alloys on step 3 confirmed the lower corrosion resistance of these materials when compared to NiTi.

### Step 2

After step 1, step 2 was started immediately. At this step, the specimens were subjected to an increasing strain, with low speed equal to  $1.5 \times 10^{-3}$  mm /s rate, during 7200s. The initial deformation value was the same value presented at the end of step 1 to each specimen. The anodic potential values were the same used in step 1. All specimens, of all materials, exhibited an increase of the anodic current during this step. The breakdown of the oxide film in this case was due to a mechanically assisted process induced by the continuous strain. Active material was exposed to the electrolyte.

NiTi specimens showed different initiation times for anodic current increase. The curves presented initially zero current value, and is stable for different times associated with each of the tested specimens, followed by a large increase in current for a short time.

No fracture occurred during this step. It is possible to follow the increasing deformation during the tests. All the specimens at the end of step 2 was into the superelasticity regime, which means the presence of martensitic structure together with austenite.

The behavior of ternary and binary alloys in this step was similar. Strain induced dissolution was observed when the passive film of the alloys was removed by the continuous deformation. Except for one of the NiTi specimens, initiation time for anodic current increase was equivalent. Similar current values were achieved for binary and ternary alloys. Localized corrosion was induced but without the fracture of the specimens. In terms of mechanically assisted film breakdown, the alloys exhibited the same behavior or corrosion resistance in the 0.9% NaCl solution. These results are shown on Figures 3, 4 and 5.

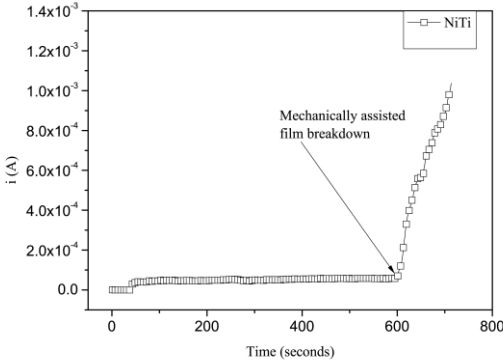


Figure 3 - Amperometric results of NiTi obtained during step 2.

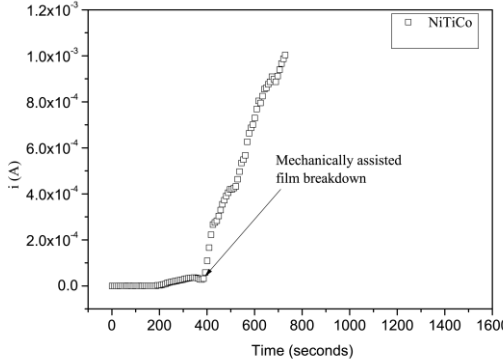


Figure 4 - Amperometric results of NiTiCo obtained during step 2.

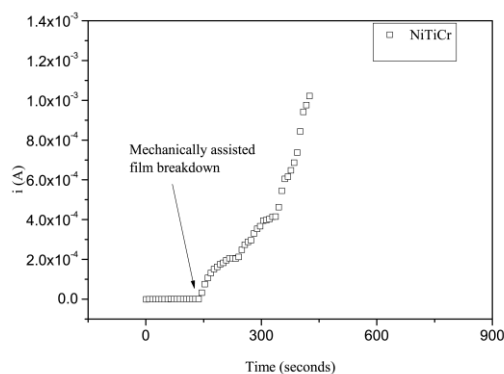


Figure 5 - Amperometric results of NiTiCr obtained during step 2.

### Step 3

Step 3 corresponds to amperometric measurements when the strain imposed stopped. With this procedure, it was possible to observe the ability of the passive film, damaged during step 2, to recover. Passive film repair or repassivation was related to the anodic current decay. When the material did not repassivate, and, as a consequence, the corrosion advances, increasing anodic current was observed, as indicate for NiTi in Figure 6. It can be observed that repassivation was not observed for NiTiCo alloy, as in Figure 7. NiTi and NiTiCr exhibited a borderline behavior, since one the specimens of each material exhibited an increasing anodic current and the other an evident repassivation associated to a sharp current decay.

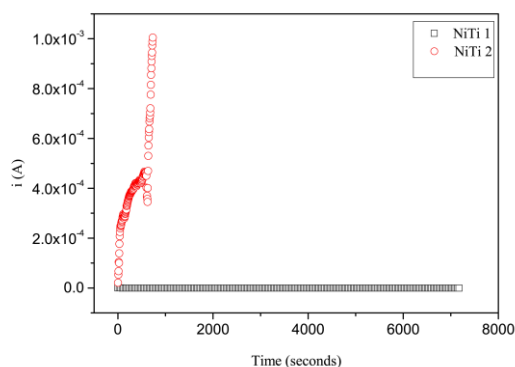


Figure 6 - Amperometric results of NiTi obtained during step 3.

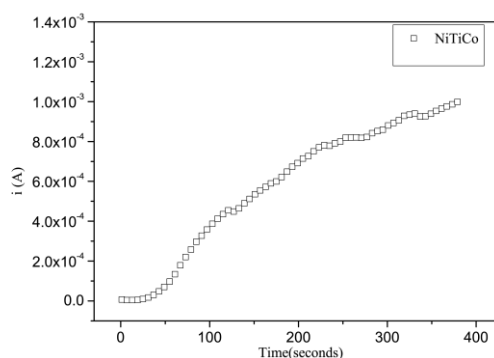


Figure 7 - Amperometric results of NiTiCo obtained during step 3.

The binary alloy showed better behavior under strain. Even when the passive film was mechanically broken, the surface presented adequate corrosion resistance and had repassivation

ability. CHAN et al [26] observed a repassivation ability of NiTi film under strain similar to the results obtained in this work. The ternary alloys presented pits in the surfaces in all steps and some specimens had fractured. The ternary alloys did not present an equivalent repassivation ability.

## Conclusions

The binary NiTi alloy presented a higher corrosion resistance when compared to ternary alloys under strain/stress in chloride environment conditions. Under constant strain the passive oxide film of the binary alloy exhibited more stable anodic current densities. This behavior was confirmed even when their protective film was mechanically removed by strain. Ternary alloys may show fracture associated with localized corrosion.

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