Supporting Information

for

Effect of Cobalt Addition on the Corrosion Behavior of Near Equiatomic NiTi Shape Memory Alloy in Normal Saline Solution: Electrochemical and XPS studies

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I. Estimation of β_a for passivation reaction (McCafferty method)

McCafferty in his valuable study entitled "Validation of corrosion rates measured by the Tafel extrapolation method" [1] demonstrated that to gain good results from the Tafel extrapolation, both the anodic and cathodic Tafel regions should be used instead of only one Tafel region.
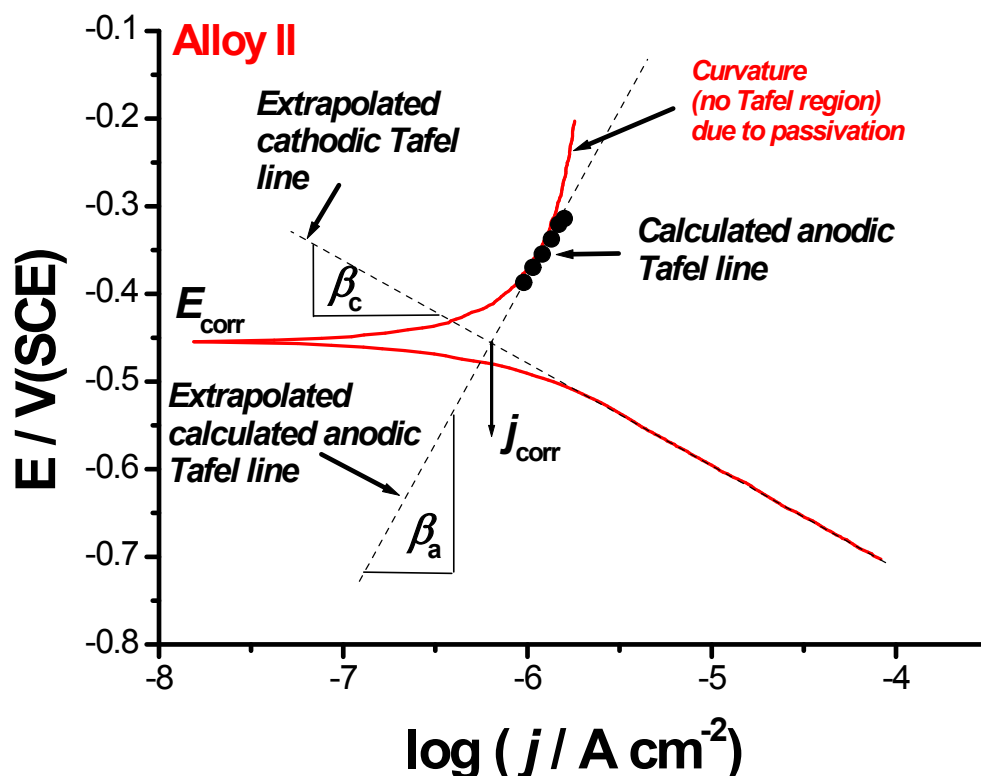

Figure S1: Analysis of Tafel regions for Alloy II to calculate the various electrochemical kinetic parameters associated with the polarization measurements presented in **Figure 3** (main manuscript).

However, the rate of corrosion can also be determined by Tafel extrapolation using either the cathodic or anodic polarization curve alone. McCafferty preferred the cathodic curve over the anodic one, as the former usually exhibits a longer, well-defined Tafel region. On the other hand, anodic polarization may deviate from the Tafel behavior exhibiting clear curvature, as noticed above, most probably due to passivation and dissolution. McCafferty reported that it is possible to calculate the anodic Tafel line from the experimental data (the recorded anodic polarization curve), as shown in **Figure S1** as a representative example for Alloy II. He postulated that extrapolation of the cathodic Tafel region back to zero overvoltage gives the net rate of the cathodic reaction at E_{corr}. This net rate of the cathodic reaction equals that of the anodic reaction at E_{corr}, see Eqs. (1) and (2) [1].

$$J_a \text{ (net experimental)} = j_a - |j_c| \qquad (1)$$

$$j_a = J_a \text{ (net experimental)} + |j_c| \qquad (2)$$

where j_a and $|j_c|$ are the calculated anodic and the cathodic current densities, respectively. Thus, j_a is the sum of the experimentally observed anodic current density (J_a) and the extrapolated cathodic current density, $|j_c|$.

The obtained Tafel slopes are depicted in Table S1.

Table S1 – Average (standard deviation) values of β_c **and** β_a for the three tested SMAs; the latter estimated using McCafferty approach [1]. Polarization measurements were conducted in 0.9% NaCl solution at a scan rate of 1.0 mV s^{-1} at 37 $^{\circ}$C

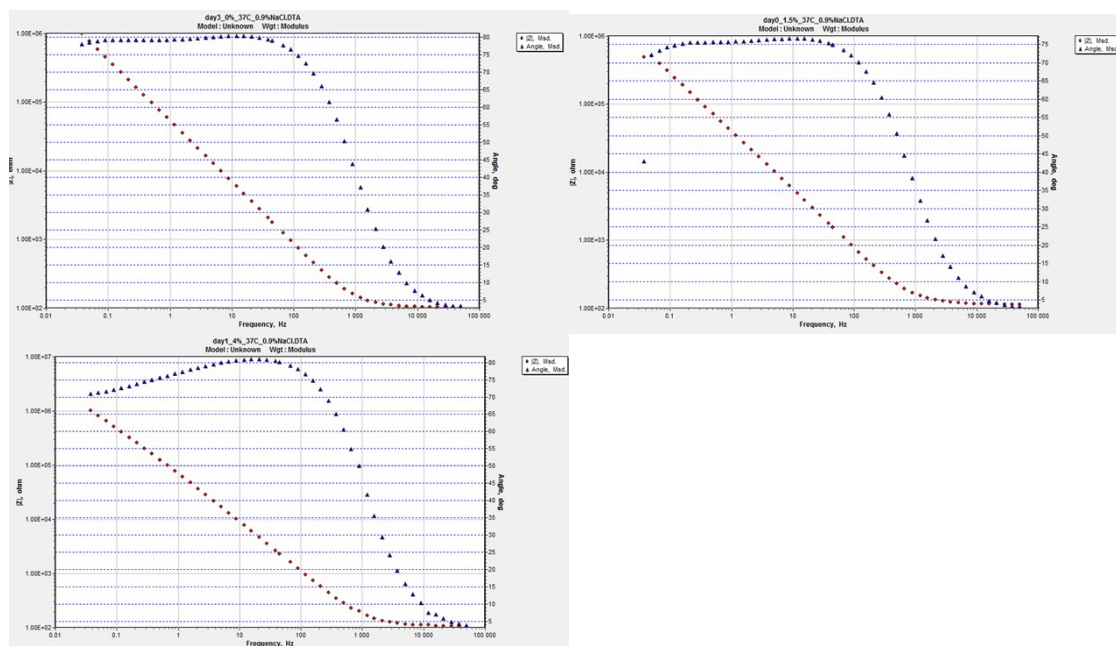| Tested alloy	β_c / mV dec^{-1}	β_a / mV dec^{-1}
Alloy I (0.0% Co)	-450(5)	716(8)
Alloy II (1.5% Co)	-118(2)	380(4)
Alloy III (4.0% Co)	-214(3)	556(5)

II. DEIS supporting data

Figure S2: Bode plots measured for day 2: top left - Alloy I, top right - Alloy II, bottom left - Alloy III
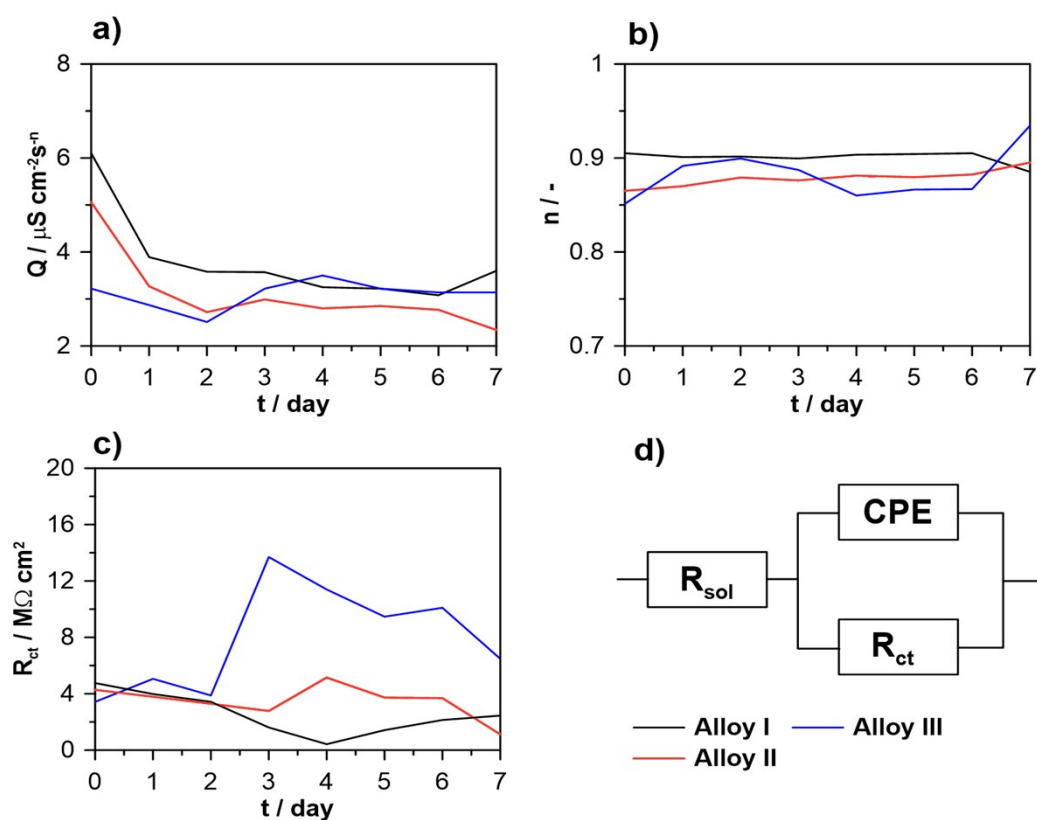

Figure S3: a-c) Variation of electric parameters CPE (Q, n) and R_{ct} obtained from fitting procedure using equivalent circuit shown on Fig 6d).
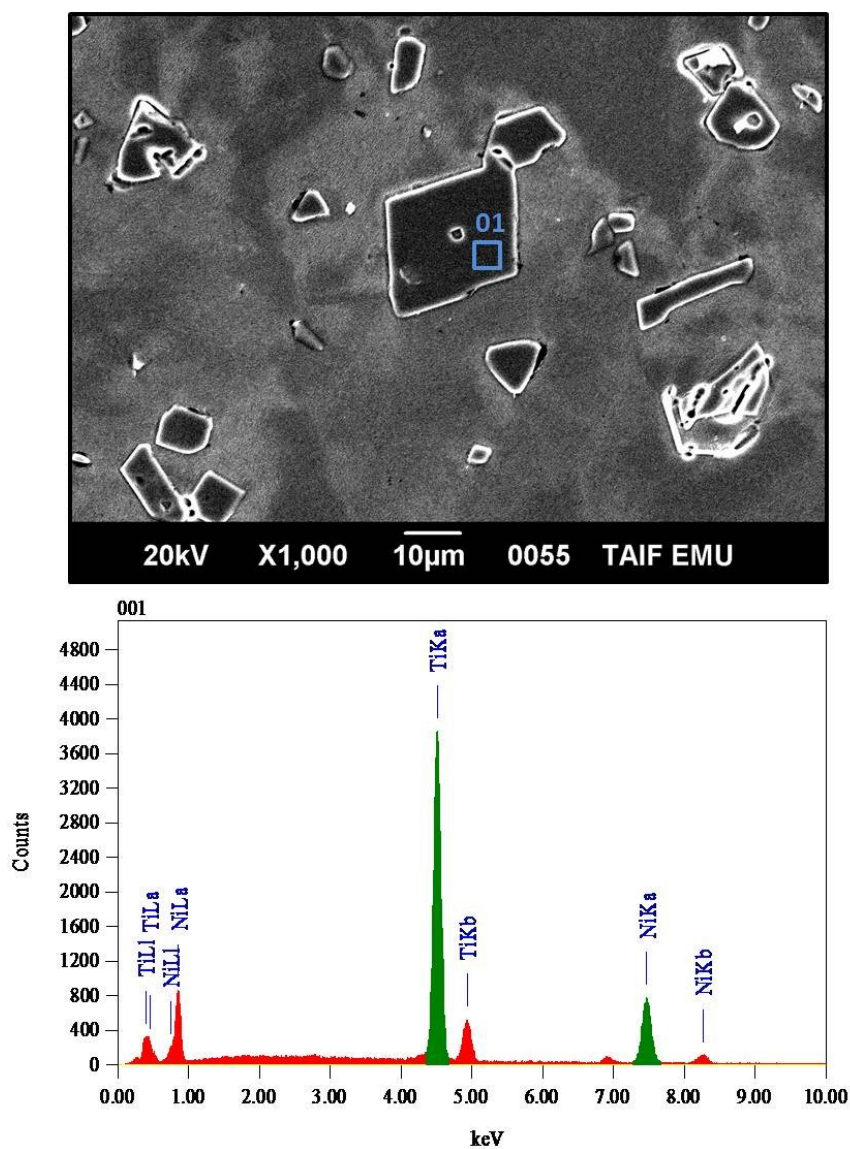
II. Supporting SEM and EDX analyses

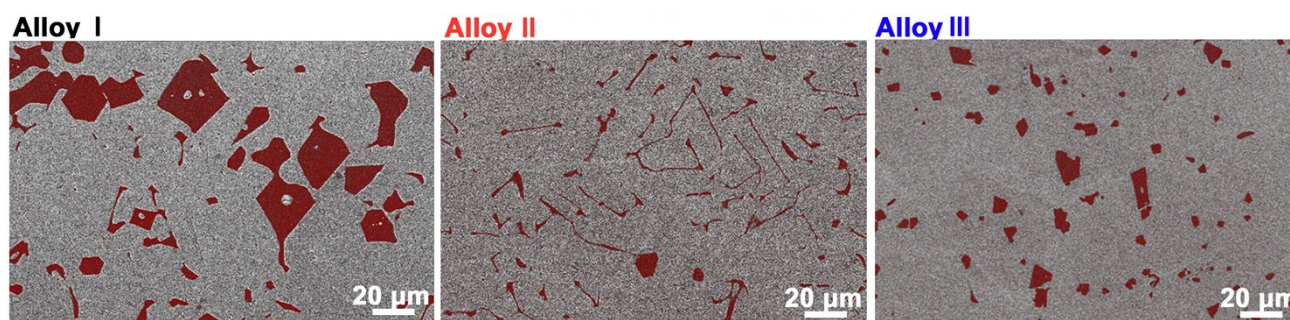**Figure S4:** SEM image and EDX spectrum of Ti$_2$Ni phase in the TiNiCo (0 at% Co) SMA.

Figure S5: SEM analysis of the studied alloys (as-polished) as a function of Co content. Alloy I: 0.0% Co; Alloy II: 1.5% Co, Alloy III**:** 4.0% Co.

EDX analysis was performed using energy-dispersive X-Ray spectroscopy (EDX) technique. EDX analysis was performed before and after 7 days exposure in 0.9% NaCl at 37 °C both for alloy matrix and within the dark phases visible on SEM micrographs. Its goal was to investigate the influence of microstructure on localized corrosion of shape-memory alloys.

The dark phases show the stoichiometry of Ti_2Ni. Here, the contribution from cobalt originates from matrix beneath the Ti_2Ni phase (due to few micron in-depth coverage of EDX). Its contribution in analyzed spectra decreases with decreasing the accelerating voltage.
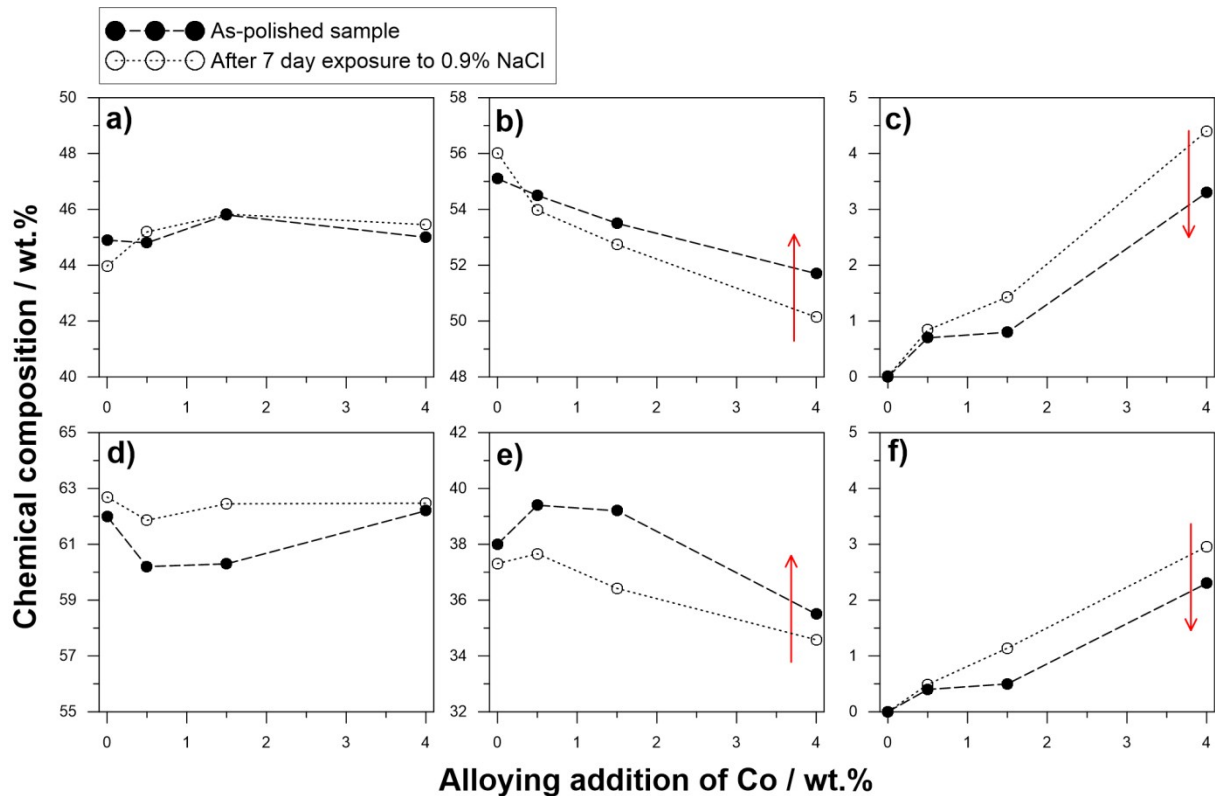

Figure S6: Changes in amount of a) titanium, b) nickel and c) cobalt in alloy matrix as a result of exposition to 0.9% NaCl solution at temperature of 37 °C. d-e) show analogous analyses carried out in the region of Ti_2Ni phase.

As a result of sample exposition to 0.9% NaCl solution at 37 °C, the amount of nickel decreases for each investigated sample. Surprisingly, the same behavior was registered within the Ti_2Ni phase, revealing no new information behind worse corrosion resistance of the NiTi SMA containing 0.5% Co. Here, the contribution from cobalt originates from matrix beneath the Ti_2Ni phase (due to few micron in-depth coverage of EDX).
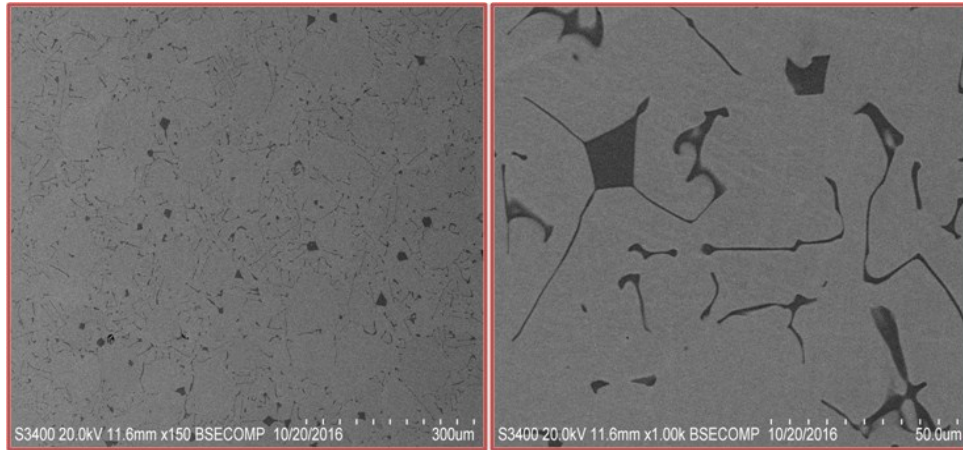
Figure S7: SEM analysis of the studied alloys after 7 days immersion in 0.9% NaCl at 37 °C as a function of Co content. Alloy I: 0.0% Co, Alloy II: 1.5% Co, Alloy III**:** 4.0% Co.
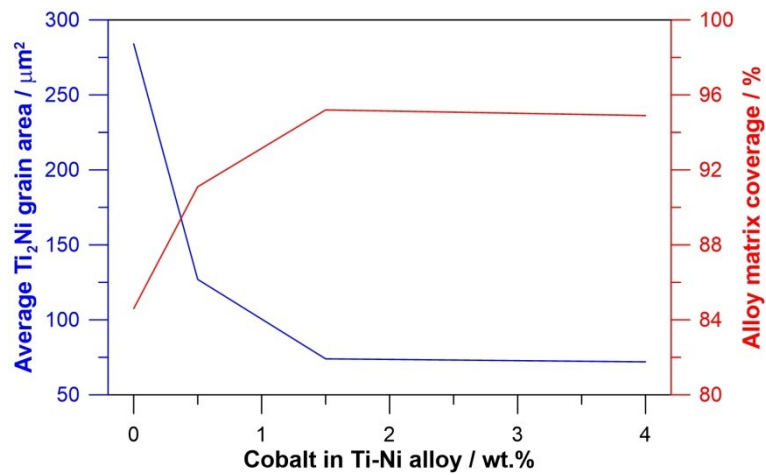

Figure S8: Variation of average grain area of the Ti_2Ni phase and matrix's surface area with Co content in the NiTi SMA. Data calculated via processing the images in Fig. 7 using Gwyddion software
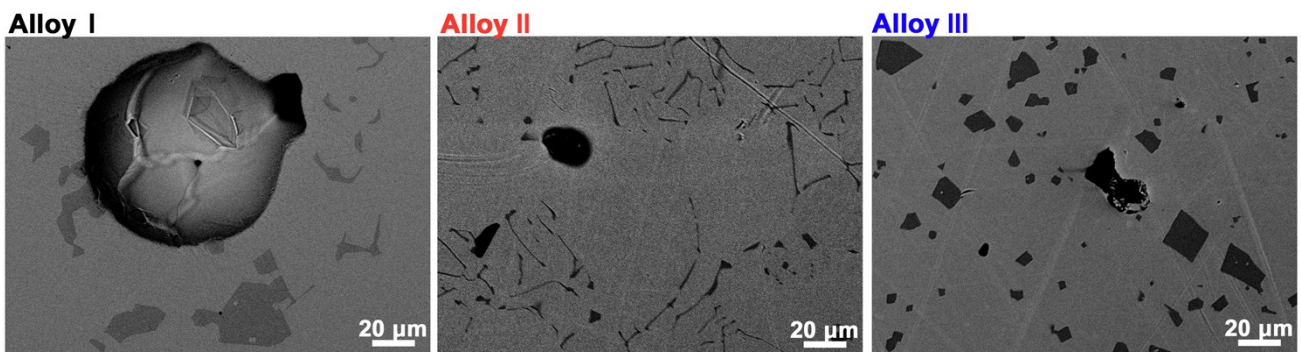

Figure S9: SEM analysis of the studied alloys after 7 days immersion in 0.9% NaCl at 37 °C as a function of Co content. Alloy I: 0.0% Co, Alloy II: 1.5% Co, Alloy III**:** 4.0% Co.

References

[1] E. McCafferty, Validation of corrosion rates measured by the Tafel extrapolation method

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