Original Article

Corrosion behaviour of sintered Ti–Ni–Cu–Nb in 0.9% NaCl environment

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\textbf{A B S T R A C T}

The uniform and localized corrosion behaviour of sintered Ti–Ni containing niobium and copper additions were studied using potentiodynamic and cyclic polarization measurements in 0.9% sodium chloride. Results indicated that copper and niobium addition did not have significant effects on the uniform corrosion characteristics, but significantly improved the pitting corrosion resistance. Both copper and niobium additions significantly increased the re-passivation potentials, while copper was observed to reduce the pitting hysteresis loop area. Alloys containing 15% copper and 2% niobium additions exhibited the most improved pitting corrosion resistance, and increased the re-passivation value from –315.60 mV to a high re-passivation potential of 840.68 mV.

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1. Introduction

Binary Ti–Ni alloys have been used extensively as shape memory components due to their relatively excellent mechanical properties, satisfying biocompatibility, unique phase transformation characteristics and excellent shape memory effect [1,2]. Due to their good mechanical properties, they find extensive use in flexibility and motion applications (e.g. peripheral stents and auto-latching control in aerospace), and are inevitably exposed to greater fatigue strains and corrosion than any other metals. The good mechanical properties of Ti–Ni alloys may be helpful in self-expanding and self-compromising applications, which make Ti–Ni easily flexible when used in medical devices. However, the risk of nickel ions release into the body can trigger allergies, and has made many professionals in the biomedical field to be cautious of its use or even reject it totally [3,4]. Nickel release from implant into the surrounding body fluid and tissue usually is accompanied by corrosion, possibly in the form of pitting, thereby reducing the mechanical performance of implants [5]. Since the demands for quality control on medical and related components used in other corrosion applications are very stringent and critical to their safe and efficient usage, the need for improving the corrosion resistance of these alloys for enhanced service performance is imperative.

It has been reported [6] that the high corrosion resistance of Ti–Ni appears to be due to the build-up of a protective TiO$_2$...
layer, which could reduce Ni ion release rate. However, these films can be easily broken down or TiO₂ film could oxidize to a less stable TiO thus accelerating corrosion of the alloy, and the formation of a new protective film becomes slower [7,8]. This can result in structural damage or equipment failure leading to production loss or corrective surgery in case of biomedical applications. Various compositional modification approaches are therefore being studied to improve the corrosion resistances of these materials. Copper base alloys are relatively cheap, and they have drawn interest due to superior electrical and thermal conductivity and improved deformation [9], which may stabilize the superelastic properties of these alloys against permanent cyclic deformation as well as reducing the stress/strain diagram hysteresis [10–13]. The addition of copper substituted for Ni in Ti–Ni to form Ti–Ni–Cu can improve localized corrosion resistance especially in 3.5% NaCl [14]. According to Bolat et al. [15], niobium addition can encourage direct translated passive state that may result in smaller values for the passive current densities thus improving the corrosion resistance of Ti–Ni alloys [16]. The addition of niobium to Ti–Ni can facilitate passivation and produce more stable passive layer by reducing anodic current density, thereby promoting corrosion resistance [15,17].

Studies on the effect of Cu addition on the corrosion behaviour of Ti–Ni have been reported [11,14,15,18,19] and the effect of corrosion behaviour of Ti–Ni with Nb addition has also been reported [15,17,20,21]. However, these studies mostly focuses on the general corrosion behaviour of Ti–Ni–Cu and Ti–Ni–Nb alloy systems, studies on the pitting corrosion behaviour of these alloys, which are prevalent in biomedical applications as well as in chloride environments where these alloys are often applied, have scarcely been reported. It was therefore decided in this study to investigate the general corrosion behaviour of Ti–Ni alloys containing copper and niobium additions in chloride environments as well as under their pitting characteristics. Varying compositions of Ti–Ni–Cu, Ti–Ni–Nb and Ti–Ni–Cu–Nb alloys synthesized through powder metallurgical process using the hot-press sintering technique were characterized using scanning electron microscope technique and their pitting characteristics were studied using open circuit potential technique, potentiodynamic polarization technique and cyclic potentiodynamic polarization technique.

2. Materials and method

2.1. Metal feedstock powders and powder preparation

Powders of pure Ti (99.5% purity and 44 μm), Ni (99.5% purity and 0.5–3.0 μm), Cu (99.0% purity and 0.5–1.5 μm) and Nb (99.0% purity and 1.0–5.0 μm) were used as starting materials. Powders with various proportions shown in Table 1 were mixed using the Turbula Shaker Mixer T2F, similar to procedure previously reported by [22], for 15 h at constant rotational speed of 49 rpm in a dry environment at room temperature.

Blended powders were consolidated using high-pressure high-temperature sintering technique at a heating rate of 20 °C/min and sintering at 900 °C with 25 min holding time. Similar to the procedure previously reported by [23], the vacuum level of the base chamber was kept less than 4.5 Pa at a constant applied uniaxial pressure of 30 Mpa. The sintered compacts pellets were allowed to cool down to room temperature at 20 °C/min, then removed for subsequent analysis. The microstructures of the sintered alloys were characterized using JEOL JSM-7600F Field Emission Electron Microscope equipped with back-scattered electron (BSE) imaging and Energy-Dispersive X-ray analysis (EDX).

2.2. Electrochemical tests

Biocorrosion tests are often conducted in saliva solution, but since Ti–Ni is mostly used for orthodontics, Rondelli and Vicentini [24] suggested that 0.9% NaCl chloride environment, which is more aggressive that saliva, can be used to simulate the body environment. Since Ti–Ni alloys are not only used for orthodontic applications, but also used for urethral, biliary and vascular stents, it is necessary to imitate different environmental conditions inside the body [11]. Electrochemical studies were therefore carried out in 0.9% NaCl environment using a three-electrode system with the sintered samples as working electrode, a graphite electrode as the counter electrode and Ag/AgCl reference electrode. The measurements were carried out with VersaSTAT 4 and Versa Studio 4 software. Potentiodynamic polarization technique was used to assess the general corrosion behaviour of the alloys while cyclic potentiodynamic polarization technique was used to determine the pitting behaviour of the alloys. Prior to scanning, all samples were immersed in the electrolytes and the cell was left for 1 h to stabilize the open circuit potential (OCP). The samples were scanned at a scan rate of 1 mV/s from −0.25 V with respect to measured OCP, and the potential was reversely scanned when a vertex potential of 1.2 V value was approached.

3. Results and discussion

3.1. The sintered composites

Typical SEM-BSE images revealing the microstructures of the polished sintered Ti–Ni alloys containing varying Cu and Nb contents are shown in Fig. 1. The microstructures revealed that copper and niobium additions had effects on the different types of phases formed. The details of characterization studies are however not reported in this study.
3.2. Electrochemical studies

3.2.1. Effects of copper additions on uniform corrosion behaviour of Ti–Ni

Typical OCP curves for the sintered alloys presented in Fig. 2a revealed that Ti–Ni alloy and alloy containing 15% copper were relatively stabilized when compared with alloys containing 5% and 10% copper addition. The stability in the potentials of Ti–Ni alloy and alloy containing 15% copper addition indicated that the alloys were thermodynamically stable with time in sodium chloride environment. From the results, the potential of Ti–Ni–10Cu alloy became stable with increase in exposure time, and was in the neighbourhood of Ti–Ni and Ti–Ni–15Cu alloys. This behaviour strongly indicates possible formation of a passive film with time. In contrast, the potential value of alloy containing 5% copper decreased with time. The potential started from −250 mV and progressed to negative potentials of about −450 mV within exposure time. The more negative potential of Ti–Ni containing 5% copper addition suggest that Ti–Ni–5Cu has a higher tendency to corrode and the decrease in potential to the negative direction indicated film breaking or dissolution of the film.

Typical polarization curve presented in Fig. 2b revealed only a slight difference on the corrosion potentials of Ti–Ni, Ti–Ni–10Cu and Ti–Ni–15Cu. Ti–Ni alloy however had a higher dissolution potential, while the dissolution potential Ti–Ni–10Cu was slightly less than the Ti–Ni–15Cu alloy, as earlier predicted from the OCP results. This behaviour indicated that the alloys had similar thermodynamic stabilities and tendencies to corrode. Similar to the OCP results, the corrosion current density of alloy containing 5% copper addition was observed to be the highest. An explanation to this unusual behaviour of Ti–Ni–5Cu alloy cannot be assertive, but may possibly be due to some heterogeneity in the alloy during sintering.

Corrosion data (corrosion potential ($E_{corr}$), corrosion currents ($i_{corr}$), and corrosion rates obtained from the polarization experiments are summarized and presented in Table 2. Results showed that the addition of copper does not improve the uniform corrosion resistance of Ti–Ni alloy. Although copper additions as indicated by polarization curves and corrosion

<table>
<thead>
<tr>
<th>Composition</th>
<th>$E_{corr}$ (mV)</th>
<th>$i_{corr}$ ($\mu$A/cm$^2$)</th>
<th>Corrosion rate (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti–Ni</td>
<td>−250.37</td>
<td>−107.71</td>
<td>0.139</td>
</tr>
<tr>
<td>Ti–Ni–5Cu</td>
<td>−87.86</td>
<td>−513.52</td>
<td>51.021</td>
</tr>
<tr>
<td>Ti–Ni–10Cu</td>
<td>−149.50</td>
<td>−582.38</td>
<td>0.359</td>
</tr>
<tr>
<td>Ti–Ni–15Cu</td>
<td>−15.28</td>
<td>−141.16</td>
<td>10.047</td>
</tr>
</tbody>
</table>
data did not result in improving the uniform corrosion resistance of Ti–Ni, it can be observed that copper addition had slight improvement on the passivity behaviour of Ti–Ni. Within the active dissolution region, copper addition resulted in increase in the corrosion currents as applied potential increased. Similar results were observed by Kassab et al. [19] and they concluded that these results suggest possible oxide layer of less protective nature formed on the Ti–Ni–Cu surface.

However, after the active dissolution, copper addition showed a significant effect on the passivity of the alloy. Beyond the active dissolution region, the corrosion currents of the alloys containing copper decreased, as compared with Ti–Ni alloy whose corrosion current increased with applied potential. The effects of copper on the passivity behaviour were more pronounced on alloys containing 10% and 15% copper, even more on the 10% copper addition.

A critical observation on the polarization curve revealed that, after the initial active dissolution region, the alloys underwent slight degree of passivity at an applied potential range between 0 and 0.2 mV. After this slight passivation, a rise in corrosion current with applied potential was observed. The rapid rise in corrosion current might possibly results from pit formation. The passivity behaviour of Ti–Ni alloy without copper addition can be explained from the fact that the pits formed after initial passivation of the alloy were very stable, as confirmed by the pits observed in the SEM images shown in Fig. 3.

### 3.2.2. Effects of niobium additions on uniform corrosion behaviour of Ti–Ni

The OCP and potentiodynamic polarization curves of Ti–Ni with 2 and 9 at.% addition of niobium are presented in Fig. 4 while the summarized corrosion data obtained from the potentiodynamic polarization are presented in Table 3. The potentials of all compositions were observed to be in steady state from the onset until the end of period of investigations. The potentials of the alloys however decreased with niobium additions. It can be generally observed from the results that the anodic current densities of Ti–Ni alloy having higher dissolution potential, rapidly increased with applied potentials.

Although niobium additions both reduce the corrosion currents and increased corrosion current densities, it was obvious that niobium additions seem to improve the passivity characteristics of Ti–Ni. It was observed that niobium addition decreased the active dissolution range, resulting in smaller values of passive current densities $i_{pass}$. By comparing the anodic corrosion current densities and the passive zone, it can be established that Ti–Ni–2Nb had improvement on the corrosion resistance properties of Ti–Ni. As compared with Ti–Ni–2Nb, the corrosion current of Ti–Ni significantly increased with applied potential. Naturally binary Ti–Ni form TiO$_2$, and with the addition of Nb, Zhao et al. [25] have earlier reported that the oxide layer formed on the Ti–Ni–Nb alloys could consists of TiO$_2$ and Nb-rich non-stoichiometric oxide layer. The additional Nb-rich oxide layer could therefore have been responsible for the corrosion resistance improvement with niobium addition.

### 3.2.3. Combined effects of niobium and copper additions on uniform corrosion behaviour of Ti–Ni

The addition of Cu and Nb as the third alloying element to binary Ti–Ni has been reported to influence its corrosion behaviour and mechanical properties [14,15,19,26]. We therefore consider it important to study and understand the electrochemical behaviour of the resultant effects of the combined addition of Cu and Nb as quaternary element on the corrosion behaviour of binary Ti–Ni produced by the specific processing technique. Results presented in Figs. 2 and 4 revealed that both copper and niobium additions improved the passivity behaviour of Ti–Ni, with 2% niobium additions having comparative improvement on the general corrosion kinetics. Further studies were therefore carried out to investigate possible synergy between copper and niobium additions, by adding 2% niobium to Ti–Ni containing varying compositions of copper.

Typical OCP and polarization curves showing the effects of Nb addition on the corrosion behaviour of Ti–Ni–Cu presented
in Fig. 5 indicated that the combination of 2% niobium with all the copper additions shifted the potential values of Ti–Ni to more positive values and decreased the current densities. The corrosion behaviour of the alloys, characterized by a partial stabilization of current density, suggests that from a potential value of 300 mV, the passive film formed were very protective. Results indicated that Ti–Ni–10Cu–2Nb was the most comparatively corrosion resistance properties (Table 4), while Ti–Ni–15Cu–2Nb displayed the most stable passive region with reduced current density. These observations suggested that Ti–Ni–Cu–Nb alloy had a better corrosion resistance than Ti–Ni and Ti–Ni–Cu alloys.

| Table 4 | Corrosion properties of Ti–Ni with varying percentages of Cu with 2 at.% Nb additions. |
|---|---|---|---|
| Composition | $E_{\text{corr}}$ (mV) | $i_{\text{corr}}$ ($\mu$A/cm²) | Corrosion rate (mpy) |
| Ti–Ni | −250.37 | −107.71 | 0.139 |
| Ti–Ni–5Cu–2Nb | −45.69 | −25.64 | 15.714 |
| Ti–Ni–10Cu–2Nb | −109.65 | −81.15 | 0.070 |
| Ti–Ni–15Cu–2Nb | 69.21 | 5.07 | 3.447 |
3.3. Pitting corrosion characteristics

Results on the individual and combined effects of copper and niobium additions on the uniform corrosion behaviour reported in the previous sections revealed copper and niobium addition did not have significant improvement on the uniform corrosion resistance of Ti–Ni, but improved its passivity behaviour. Owing to the fact that electrochemical phenomena in chloride environments is often localized, further studies on the effects of niobium and copper on the corrosion behaviour of Ti–Ni was therefore investigated using cyclic potentiodynamic polarization technique to assess the susceptibility of the alloys to pitting. Scanning was carried out at a scan speed of 1 mV/s from −0.25 V and reversed at 1.2 V. The resulting cyclic polarization curves are presented in Figs. 6 and 7, while the pitting corrosion data obtained are summarized in Table 5.

3.3.1. Effects of copper addition

The cyclic polarization scans showing the effects of copper on the pitting behaviour of Ti–Ni presented in Fig. 6 showed that an increase in copper addition shifted the pitting potentials of the alloy to higher values and decreased the hysteresis. It can be observed from Table 5 that alloy containing 5% copper addition displayed comparatively highest pitting potential, but with relatively lower re-passivation potential. Although the pitting potential of alloys containing 10% and 15% copper were
Fig. 7 – Cyclic potentiodynamic potential curves of (a) Ti–Ni, (b) Ti–Ni–2Nb, (c) Ti–Ni–6Nb and (d) Ti–Ni–9Nb in sodium chloride.

Fig. 8 – SEM images of cyclic polarized (a) Ti–Ni, (b) Ti–Ni–2Nb, (c) Ti–Ni–6Nb and (d) Ti–Ni–9Nb.
lower than alloy containing 5% copper, their re-passivation potentials were significantly higher. Increasing copper addition significantly increased the re-passivation potentials and reduced the hysteresis loop. These observations have been previously reported, and were attributed to possible Cu$^{2+}$ ions release and re-deposition as Cu inside the active sites thus raising the potential within the pit (or crevice) [14,23]. Careful observations on nature of the pits formed on binary Ti–Ni with and without copper additions as shown in Fig. 6 indicated that the pits formed were localized and that the pits formed seem to decrease with increasing amount of Cu additions.

### 3.3.2. Effect of niobium addition

The cyclic polarization curves showing the effects of niobium of the pitting corrosion behaviour of Ti–Ni are presented in Fig. 7. Results indicated that an increase in niobium addition shifted the pitting potentials of Ti–Ni to higher values and enhanced its protection capability. Increasing niobium addition significantly increased the re-passivation potentials and reduced the hysteresis loop. Ti–Ni with 9% Nb displayed the comparatively highest pitting potential, and relatively higher re-passivation potential.

The measured pitting potential values presented in Table 6, suggested that pitting occurred at higher potential as Nb content increases. Furthermore, the re-passivation was also favoured by increasing Nb. The summarized protection potential values validated the observed hysteresis areas in Fig. 7, while the images presented in Fig. 8 corroborated the summarized potential values and cyclic curves, and confirmed that pits decreased as Nb increases. The ability of the Ti–Ni to re-passivate at higher potentials in the presence of Nb could indicate that the Nb-rich film formed might have protected the alloy from accelerated dissolution.

### 3.3.3. Combined effects of niobium and copper additions

Cyclic polarization curves showing the combined effects of copper and niobium additions on the pitting behaviour of Ti–Ni alloy is presented in Fig. 9. Results indicated that adding both copper and niobium had synergistic effects on pitting behaviour. Pitting corrosion data obtained as shown in Table 7 revealed that alloy containing 2% niobium and 10% copper additions displayed the most outstanding pitting resistance. The increasing re-passivation potential values with increasing copper content are related to the decrease in the numbers

### Table 5 – Effects of copper addition on the pitting corrosion data of Ti–Ni.

<table>
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<tbody>
<tr>
<td>$E_{\text{pass}}$ (mV)</td>
<td>$-306.40$</td>
<td>$-607.89$</td>
<td>$-593.48$</td>
<td>$-582.74$</td>
</tr>
<tr>
<td>$E_{\text{pit}}$ (mV)</td>
<td>$314.99$</td>
<td>$779.65$</td>
<td>$398.10$</td>
<td>$335.54$</td>
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<tr>
<td>$E_{\text{re-pass}}$ (mV)</td>
<td>$-358.23$</td>
<td>$134.95$</td>
<td>$149.67$</td>
<td>$180.65$</td>
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<tr>
<td>$E_{\text{pit}} - E_{\text{pass}}$</td>
<td>$621.39$</td>
<td>$1387.54$</td>
<td>$991.59$</td>
<td>$918.28$</td>
</tr>
<tr>
<td>$E_{\text{pit}} - E_{\text{re-pass}}$</td>
<td>$673.22$</td>
<td>$644.70$</td>
<td>$248.44$</td>
<td>$154.89$</td>
</tr>
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</table>

### Table 6 – Pitting potential and re-passivation potentials of Ti–Ni with Nb additions.

<table>
<thead>
<tr>
<th></th>
<th>Ti–Ni</th>
<th>Ti–Ni–2Nb</th>
<th>Ti–Ni–6Nb</th>
<th>Ti–Ni–9Nb</th>
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<tbody>
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<td>$E_{\text{pass}}$ (mV)</td>
<td>$-306.40$</td>
<td>$-525.30$</td>
<td>$-458.83$</td>
<td>$-525.39$</td>
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<td>$E_{\text{pit}}$ (mV)</td>
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<td>$369.27$</td>
<td>$354.25$</td>
<td>$481.53$</td>
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<tr>
<td>$E_{\text{re-pass}}$ (mV)</td>
<td>$-358.23$</td>
<td>$72.38$</td>
<td>$80.66$</td>
<td>$193.53$</td>
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<tr>
<td>$E_{\text{pit}} - E_{\text{pass}}$</td>
<td>$621.39$</td>
<td>$896.57$</td>
<td>$813.08$</td>
<td>$1006.26$</td>
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<tr>
<td>$E_{\text{pit}} - E_{\text{re-pass}}$</td>
<td>$673.22$</td>
<td>$269.89$</td>
<td>$273.59$</td>
<td>$288.00$</td>
</tr>
</tbody>
</table>
Table 7 – Pitting potential and re-passivation potentials of Ti–Ni–Cu with Nb additions.

<table>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{pass}}$ (mV)</td>
<td>−306.40</td>
<td>−493.49</td>
<td>−629.05</td>
<td>−549.31</td>
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<tr>
<td>$E_{\text{pit}}$ (mV)</td>
<td>314.99</td>
<td>−177.89</td>
<td>143.23</td>
<td>126.98</td>
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<tr>
<td>$E_{\text{re-pass}}$ (mV)</td>
<td>−358.23</td>
<td>80.66</td>
<td>232.18</td>
<td>291.37</td>
</tr>
<tr>
<td>$E_{\text{pit}} − E_{\text{pass}}$</td>
<td>621.39</td>
<td>315.60</td>
<td>861.23</td>
<td>840.68</td>
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<tr>
<td>$E_{\text{pit}} − E_{\text{re-pass}}$</td>
<td>673.22</td>
<td>−258.55</td>
<td>88.95</td>
<td>164.39</td>
</tr>
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</table>

Fig. 10 – SEM cyclic images of (a) Ti–Ni, (b) Ti–Ni–5Cu–2Nb, (c) Ti–Ni–10Cu–2Nb and (d) Ti–Ni–15Cu–2Nb.

and sizes of the pits on the surface (Fig. 10) of the tested sample.

4. Conclusions

Based on the results obtained, the following conclusions can be drawn:

- Copper addition improved the corrosion resistance of the alloy to general and localized corrosion such as pitting, while niobium improved passivity and shifted the potential to more positive values.
- The combination of copper and niobium resulted in passive formation at higher potentials, and the passive region was observed to be stable.
- Pitting and re-passivation potentials increased with both copper and niobium addition thus leading to reduced pitting hysteresis area.
- At the lowest passivation potential −629.05 mV, relatively high pitting potential of 232.18 mV and high re-passivation potential at 861.23 mV, Ti–Ni–10Cu–2Nb alloy depicts improved pitting corrosion resistance.

Conflicts of interest

The authors declare no conflicts of interest.

REFERENCES


