Investigation of dual phase (β+γ) CoNiAl MSMA Microstructure effect on the Mechanical Properties and Bio-Corrosion Resistance

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ABSTRACT
In this study five compositions of CoNiAl alloy with fixed Al content were prepaid to investigate the effect of chemical composition on the microstructure and phase volume fractions. It was found that by increasing Co the volume fraction of β phase increases and by increasing the β phase the grain size will be increased. This increase will be reflected on increasing the hardness of this alloy. Further investigations for the corrosion resistance in simulated body environment were done. It was found that phase volume fractions increased corrosion rate by increasing the volume fraction of β phase.

Keywords: Co Ni Al, Bio-Medical Corrosion, Hardness, Microstructure

INTRODUCTION
The new ferromagnetic shape memory CoNiAl alloy system are considered as alternative alloy for the expensive brittle well known NiMnGa due to their better ductility and a lower cost of constituent elements. The origin of good ductility came from the presence of γ phase precipitates at grain boundaries of β phase [1, 2].

In general, the investigation of microstructure control in Co-Ni-Al alloys is focusing on (1) the grain size of the β phase and (2) the volume fraction and distribution of the precipitates [3, 4]. Several studies have been devoted to this attractive field. Tanaka et al. investigated the quantitative effect of the γ phase on the mechanical and shape memory properties by annealing treatment [5]. Kainuma et. al. [3] pointed out that the dendritic structure is not favorable for hot-workability. The β phase in a limited composition range experiences a martensitic transformation to a L1₀ structure on cooling. It is the active phase for shape memory effect. However, it has been found that the presence of the γ phase affects the martensitic transformation behavior of the β phase and, at the same time, enhances the ductility of the matrix.
Whilst enhancing the mechanical applicability of the alloys due to the latter effect, γ phase reduces the shape memory functionality of the alloys by suppressing their martensitic transformation. Therefore, for optimizing the microstructural design of the alloys, it is necessary to understand the phase formation, phase stability and phase properties of Co-Ni-Al alloys [6, 7].

This study was focused on the effect of Co and Ni on β and γ volume fractions and grain size of β phase on the mechanical properties of this alloy presented by Vickers Hardness.

**Experimental Work:**

Five polycrystalline ingots with different compositions of pure element of 99.9% electrical Co Ni and Al were prepared. The first four samples were prepared with a fixed Al Atomic percent of 28% the last sample was with 25% as presented in Table (1). All samples were melted 4 times by ARC melting for homogenization. The compositions of the four alloys prepared according to the samples were annealed at 1200°C in a sealed quartz tube and subsequently quenched in ice water for periods of (6 and 12 h). All samples were optically investigated and digitally analyzed by sophisticated software (Image J2X). All samples were characterized by X-ray diffraction (XRD) and analyzed by SEM with EDAX. The hardness values were determined by Vickers Micro hardness. A human body simulated corrosion sell was designed to represent the biomedical application environment. Ringer solution was used at 37°C. Tafel curves were investigated using potentiostate instrument.

**Results and Discussion**

The microstructure and chemical analysis of samples were presented in Table (1). Where it was found that the structure of these alloys consisted of two main phases (β and γ) where the β phase presented with in the structures with two forms (β and β’ or M). The γ phase was precipitated at the grains boundaries of β grains as shown in Figure (1). All samples were investigated and digitally analyzed by computer to determine the phase volume fractions and grain size.
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All samples investigated by SEM supported with EDAX and XRD in order to investigate the microstructure an analysis the chemical compositions of both phases as presented for one of the samples. Where it was found by analyzing the first four samples that there was two different chemical composition all over the sample one of them are rich with Aluminum which presented the β phase and the other was rich with cobalt represented the γ phase [4]. The chemical analysis showed the chemical analysis of each phase for 1st group of samples. While only β phase compositions for last two samples were determined.

The volume fractions grain size and hardness values were presented in Table (1). All volume fraction and grain size has been determined by using Image J 2X software. According to these results it could be found that the volume fraction of β phase was increased by increasing the heat treatment time and by increasing the volume fraction the grain size of β grains was also increased as presented in Table (1) regarding Samples CO1, CO2 and CO5 when compared after treatment for 6 hours and 12 hours respectively. In addition to the effect of heat treatment it was found that the chemical composition also effected on the volume fraction and the grain size of β phase that will effect by increasing the hardness values.

Table (1) the chemical analysis and hardness values for the alloys with different heat treatment periods and the phase’s volume fractions and grain size for each case.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Alloy</th>
<th>β Analysis (at%)</th>
<th>γ Analysis (at%)</th>
<th>Annealing time (h)</th>
<th>β%</th>
<th>GS µm</th>
<th>Hv</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Co</td>
<td>Ni</td>
<td>Al</td>
<td>Co</td>
<td>Ni</td>
<td>Al</td>
</tr>
<tr>
<td>CO1</td>
<td>Co35Ni37Al28</td>
<td>35</td>
<td>39</td>
<td>26</td>
<td>42</td>
<td>39</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12</td>
<td>52</td>
<td>60</td>
<td>56</td>
<td>61</td>
<td>21</td>
</tr>
<tr>
<td>CO2</td>
<td>Co36Ni36Al28</td>
<td>32</td>
<td>37</td>
<td>31</td>
<td>43</td>
<td>37</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12</td>
<td>58</td>
<td>65</td>
<td>56</td>
<td>61</td>
<td>21</td>
</tr>
<tr>
<td>CO3</td>
<td>Co37Ni35Al28</td>
<td>35</td>
<td>35</td>
<td>30</td>
<td>44</td>
<td>34</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12</td>
<td>80</td>
<td>75</td>
<td>71</td>
<td>80</td>
<td>18</td>
</tr>
<tr>
<td>CO4</td>
<td>Co38Ni35Al28</td>
<td>36</td>
<td>34</td>
<td>30</td>
<td>45</td>
<td>37</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12</td>
<td>55</td>
<td>30</td>
<td>45</td>
<td>40</td>
<td>25</td>
</tr>
<tr>
<td>CO5</td>
<td>Co37Ni38Al25</td>
<td>26</td>
<td>39</td>
<td>35</td>
<td>45</td>
<td>37</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12</td>
<td>55</td>
<td>30</td>
<td>45</td>
<td>40</td>
<td>25</td>
</tr>
</tbody>
</table>
Figure (2) showed the effect of β phase volume fraction on hardness. According to the increase in grain size it was indicated that the amount of the ductile γ phase around the grain boundaries will be reduced as shown in Figure (4).

The ductile phase when precipitated around the grains of β phase will work as a dumper for external forces when applied on the grains that will minimize the effect of hardness indenter on the β grains accordingly the hardness will be reduced. These results were explained more through Figure (5) were by increasing β volume fraction that hardness will increase.

By investigation the corrosion behavior of CO5 samples that were treated for 6 and 12 hours in a simulation body environment. The corrosion behavior was explained through the TAFEL curves.

Figure (6 A & B) showed TAFEL Curves. According to TAFEL curves determinations that presented in Table (2). The corrosion rate was increased by increasing the volume fraction of β phase. That because the β phase which presented as martensite phase is a stressed phase which will be preferred to behave as an anode.

Table (2) Corrosion behavior parameters for CO5T1 and CO5T2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Area cm²</th>
<th>β %</th>
<th>G.S µm</th>
<th>I corr µA/cm²</th>
<th>E corr mV</th>
<th>CR MMPY</th>
<th>I pp µA/cm²</th>
<th>E pp mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO5T1</td>
<td>0.28</td>
<td>45</td>
<td>28</td>
<td>5</td>
<td>-650</td>
<td>0.12</td>
<td>1.2</td>
<td>-620</td>
</tr>
<tr>
<td>CO5T2</td>
<td>0.21</td>
<td>50</td>
<td>30</td>
<td>0.69</td>
<td>-990</td>
<td>0.33</td>
<td>0.9</td>
<td>-1010</td>
</tr>
</tbody>
</table>

Figure (3) The effect of β Volume fraction on Vickers Hardness

Figure (4) The Relation Between the grain size of β phase and the volume fraction of γ phase

Figure (5) The relation between the grain size of β phase and hardness values.
The calculation of corrosion rate have been done depending on Icorr and according to ASTM Standards G102 as shown in equation below [8]:

$$CR = \frac{I_{corr} \cdot K \cdot EW}{dA}$$

Where: EW is equivalent weight for the alloy according to its chemical compositions. d is the Density, and A is the sample area. While K is a constant depends on the unit of corrosion rate.

**Figure (6) Tafel Curves for (A) CO5T1 and (B) CO5T2**

The cyclic corrosion curves that were presented in Figure (7 A & B) it was found that area between the two anodic curves indicated that there is no possibility for pitting corrosion for both treatments.

**Figure (7) The cyclic corrosion curves for (A) CO5T1 and (B) CO5T2**
CONCLUSIONS
1- The microstructure was consisted of two main phases (β and γ) where the β phase presented with two forms. These forms were Austenite phase (β) and the Martensitic Phase (M or β').
2- Increasing the heat treatment time will increase both the volume fraction and grain size β phase.
3- The volume fraction and grain size of β phase increasing the increasing Co at% decreasing Ni At%.
4- The increase in γ phase will be related to decreasing in β phase grain size.
5- The increase in β grain size will increase the values of Vickers hardness.
6- The corrosion rate increased with increasing on the volume fraction of β phase moreover.

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