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Improving of the surface properties of NiTiCu shape memory alloy by oxidation

NiTiCu şekil hatırlamalı alaşımın oksidasyon ile yüzey özelliklerinin geliştirilmesi

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ABSTRACT

NiTi and NiTi-based shape memory alloys are so often used in medical applications to show that thermoelastic martensitic transformation. The major disadvantage of these alloys although advantageous, is the element nickel in the alloy. Alloy used as implants in the body, nickel element may be harmful to the body by mingling blood. Many methods have been applied to eliminate this detrimental effect. One of these methods is to create a barrier oxide by oxidizing the surface of the alloy. Therefore, at 800, 900 and 1000 °C temperature, the oxidation process was applied on NiTiCu shape memory alloy which transforms at body temperature. After this oxidation process results, the oxidation rate constants for oxidation of indicator were increased. As a result of the SEM-EDX measurements, Nickel was found to be minimal on the surface of alloy. The Changes occurring in the transition temperature of the alloy subjected to the oxidation process were measured by Differential Scanning Calorimetry (DSC). The ideal transformation was observed in alloys oxidized at 900 °C.

Keywords: Shape memory alloy, Implant, Oxidation

ÖZET

NiTi ve NiTi bazlı şekil hatırlamalı alaşımlar termoelastik martenzitik dönüşüm gösterdiği için medikal uygulamalarda sıklıkla kullanılırlar. Bu alaşımlar avantajlı olmasına rağmen en önemli dezavantajı, alaşım içindeki Nikel elementidir. Vücut içinde implant olarak kullanılan alaşımda, Nikel elementi kana karışarak vücuda zaralı olabilir. Bu zararlı etkiyi yok etmek için birçok yöntem uygulanmıştır. Bu yöntemlerden biri alaşımının oksitleyerek yüzeyinde oksit bir bariyer oluşturmaktır. Bu nedenle Vücut sıcaklığında dönüşüm veren NiTiCu şekil hatırlamalı alaşıma 800, 900 ve 1000 °C de oksidasyon işlemi uygulanmıştır. Bu oksidasyon işlemi sonucu, oksitlenme hızını göstergesi olan oksidasyon sabiti değerinin sıcaklık artıkça artığı görülmüştür. Alaşımların SEM-EDX ölçümleri sonucunda yüzeyinde Nikel elementinin çok az olduğu görüldü. Oksidasyon işlemine tabi tutulan alaşımların dönüşüm sıcaklığında meydana gelen değişim Diferansiyel Taramalı Kalorimetre (DSC) ile ölçüldü. En ideal dönüşüm 900 °C de oksitlenen alaşımda görüldü.

Anahtar sözcükler: Şekil hatırlamalı alaşım, İmplant, Oksidasyon

Introduction

NiTi alloys are often used in medical devices as elastic material due to their compression and expansion properties. However, nickel ions can create a potential risk for human body. Therefore this risk has to be eliminated in the use of medical applications. Nickel can be released into the body from the implant materials. The medical quality of these materials could be improved by increasing their corrosion resistance (1-4). The TiO2 layers on surface of alloys require to be increased, in order to enhance the high corrosion resistance of NiTi alloys. The various modifications in the alloy composition can

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improve the corrosion resistance (2,5,6). Also, the surface modification plays an important role for improving the corrosion resistance of NiTi alloys. Recently, laser oxidation, ion implantation and thermal treatment are applied on alloy's surface (6-7). In addition, anodizing, coating or polymer materials and the HAP prevent the penetration of nickel into the body (7). Ti elements in NiTi alloy are quickly oxidized and will be created a serious barrier in front of Ni ions. The surface roughness, homogeneous league, tailings, and the geometry of space prevent to be sustained of the titanium oxide layer (8).

In this study, oxidation behavior of The NiTiCu shape memory alloy which show transformation at body temperature will be studied.

Experimental

NiTi shape memory alloys with %5 at. Cu element was produced by using powder elements at high purity levels(%99.9). The powders of elements were made into pellet, and melted at arc melter furnace in vacuum atmosphere. The melting was done five times to ensure homogenization. The experimental samples were prepared by cutting from bulk alloy. To determine transformation of NiTiCu alloy, Differantial Scanning Calorimetry (DSC) measurement was done. Oxidation parameters of this alloy for different oxidation temperature were calculated from TG/DTA (Thermogravimetric) measurement curves. The oxide on NiTiCu alloys were determined by EDX measurement.

Results and Discussions

The transformation temperatures of NiTiCu alloy were determined by Differential Scanning Calorimetry (DSC) measurement. DSC measurement was done at the -40 and 100 °C temperature ranges with the 10 °C /min heating-cooling rate. Result of DSC as graph can be seen in Figure 1.

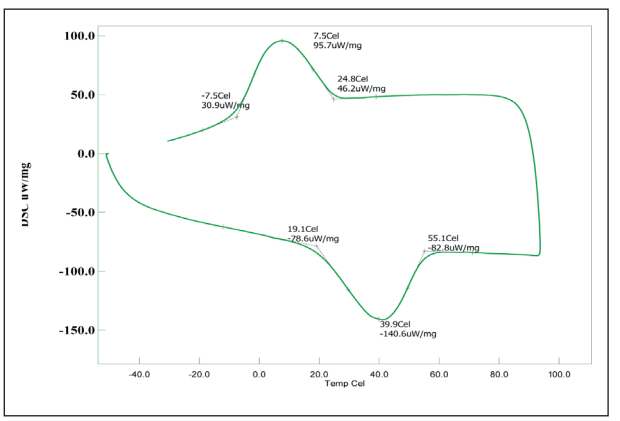


Figure 1: DSC result of NiTiCu shape memory alloy.

In Figure 1, As (Austenite Start) temperature is 19.1 °C, Af (Austenite Final) temperature is 55.1 °C, Ms (Martensite Start) temperature is 24.8 °C and (Martensite Final) temperature is -7.5 °C. These temperature values can be ideal for human body (at 37 °C). These results are similar as Essoni study (9). They found transformation temperature value of NiTi%7Cu alloy about human body temperature. The differences Essoni study from us, R phase was seen in their study.

After determining transformation temperature, oxidation procedure was applied to alloy for 800,900 and 1000 °C. The oxidation procedure can be explained as follow: First step; the alloys were heated to (isothermal oxidation temperatures) 800, 900 and 1000 °C in nitrogen atmosphere by fastly (heating rate of 50 °C/min.) via TG/DTA device. Second step; at isothermal oxidation temperature, the atmosphere was changed as oxygen and alloys was exposed oxygen during 210 minutes.

The effect of oxygen at constant (800,900 and 1000 °C) oxidation temperatures can be seen thermogravimetric curve in Figure 2. By increasing time, gained mass of NiTiCu alloys was increased by logarithmically at isothermal temperatures. The meaning of mass gain is the penetration of oxygen into the alloy. The maximum penetration of oxygen amount was seen at 1000 °C oxidation temperature.

As seen from Fig. 2, the curve of the mass gain increase is parabolic. This figure gives information about the mass gain per area at constant temperature. Parabolic isothermal oxidation constant (K_p) was calculated by follow equation:

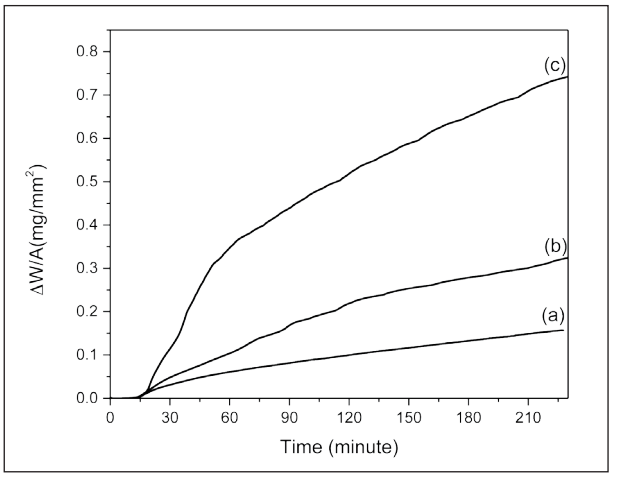


Figure 2: Mass gain graphs of NiTiCu alloys with different oxidation temperatures (a-800 °C, b-900 °C, c-1000 °C) in the oxygen atmosphere.

$$\frac{\Delta W^2}{A} = K_p t \quad (1)$$

The slope of the $(\Delta W/A)^2$ vs. (t-time) graph gives the value of the oxidation constant (K_p). K_p values calculated from the curve of the graph are given in Table 1. As the correlation constant given in the Table is between 0.90-0.99, it can be stated that oxidation of NiTiCu alloy obeyed the parabolic law (10-11).

Table 1. Oxidation constant values of NiTiCu shape memory alloy

Oxidation Temperature	Kp ($mg^2\ mm^{-4}\ s^{-1}$)	R^2
800 °C	1.88×10^{-6}	0.99
900 °C	2.47×10^{-5}	0.97
1000 °C	5.39×10^{-5}	0.93

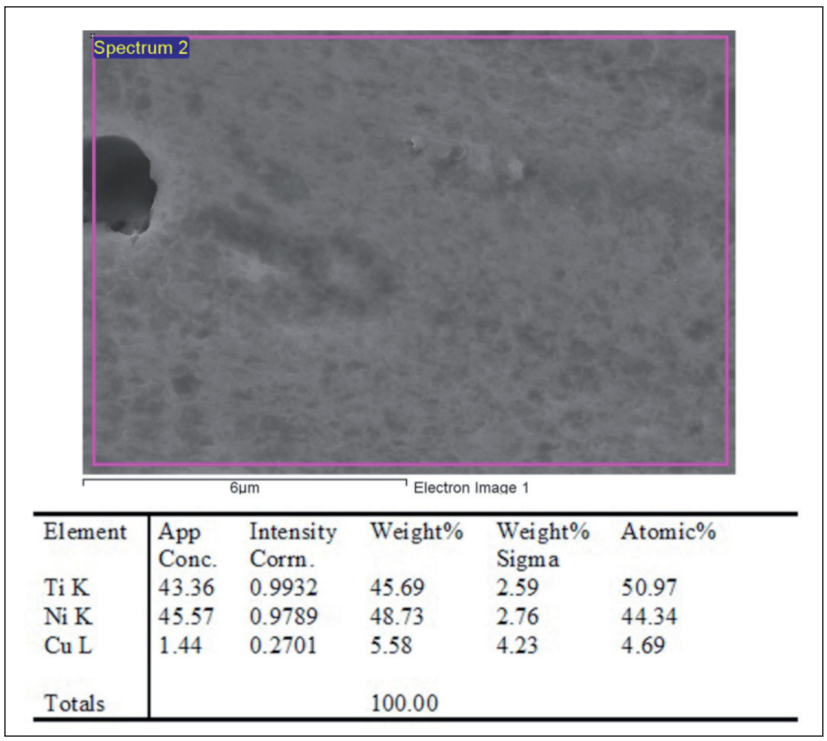
Most alloys are oxidized by the oxygen in air by heated of nonheated. This process is called corrosion. Electrons in alloys leap from the metal to the oxygen molecules. The negative oxygen ions which are thus formed penetrate into the metal, causing the growth of an oxide surface (12).

Because of comparing nonoxide and oxide NiTiCu shape memory alloys, SEM image and EDX result was given in Figure 3.

In Fig. 4., EDX results of NiTiCu alloys can be seen for two point. According to EDX results, Nickel amount on surface is %1.95 in atomic. This value is very little than in other elements value. It can be said that, oxidation at 900 °C eliminated effect of Ni element on the surface of NiTiCu alloy. The reason of decreasing Ni amount can be explained as other elements of alloys. Ti and Cu elements show more activation with oxygen.

Figure 5 shows EDX result of NiTiCu alloy which exposed oxygen at 1000 °C. EDX result of this oxidation temperature almost similar to 900 °C. Nickel amount of on surface of alloys is very small. This result can be showing that oxidation of NiTiCu eliminated harmful property of Nickel element.

Figure 6 shows that DSC Thermograms of NiTiCu alloys after oxidation. The transformation temperature of NiTiCu alloy affected from Oxidation temperature at 1000 °C. The alloys do not show transformation. At 800 °C oxidation temperature, transformation temperature curve of alloy is not well. The transformation temperature curve and value of alloys is ideal for 900 °C oxidation temperature. For the samples oxided at 1000 °C, it can be said that all of dislocations will be eliminated thermoelastic behavior of NiTiCu alloy. Moreover, precipitates starts to dissolve in the matrix and transformation temperatures decrease (13). For 1000 °C oxide alloy, The dislocation and dissolving precipitates may be reasons more Ni element than oxide NiTiCu alloy at 900 °C.



Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
Ti K	43.36	0.9932	45.69	2.59	50.97
Ni K	45.57	0.9789	48.73	2.76	44.34
Cu L	1.44	0.2701	5.58	4.23	4.69
Totals			100.00		

Figure 3: General EDX result of nonoxide NiTiCu alloy.

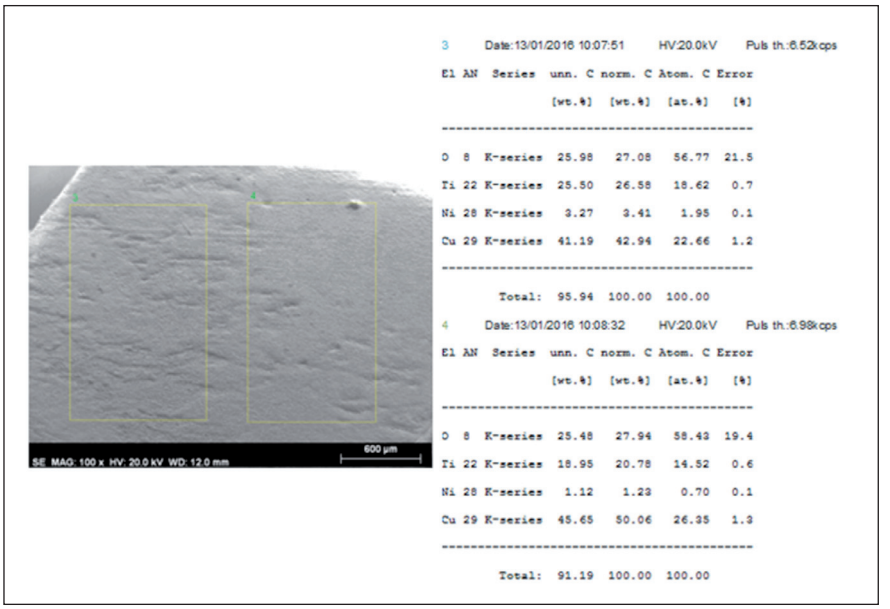


Figure 4: EDX result of NiTiCu alloys which exposed oxygen at 900 °C.

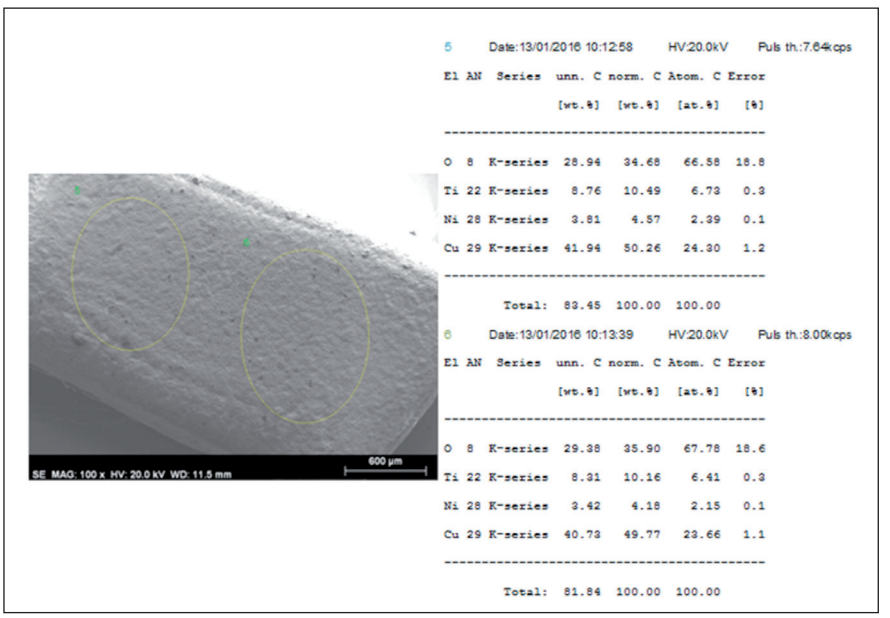


Figure 5: EDX result of NiTiCu alloy which exposed oxygen at 1000 °C.

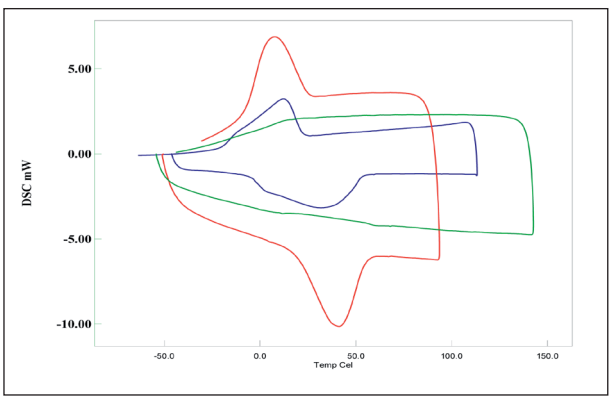


Figure 6: DSC Thermograms of NiTiCu alloys after oxidation (blue line: oxidation at 800 °C, red line: oxidation at 900 °C, oxidation at 1000 °C).

Conclusions

The oxidation behavior of NiTiCu alloy are summarized as below,

- The oxidation constant values of NiTiCu alloy increased by rising temperature.
- After the oxidation, surface of alloy was covered by Oxygen. Thus the toxicological effects of nickel prevented.
- Oxidation temperature value influenced to transformation temperature of alloy. There was no transformation at 1000 °C oxidation temperature.

Acknowledgements

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References

1. Kaczmarek M., Corrosion resistance of NİTİ alloy in simulated body fluids, Archives of Materials Science and Engineering, 28,(2007),269-272
2. Lethabena M.L., Olubambi P.A., Chikwanda H.K., Corrosion behaviour of sintered TiNiCuNb in 0,9 % NaCl enviroment, J. Materials Research Technology (2015),1-10
3. Mareci D.,Chelariu R.,Cailean A. and Sutiman D.,Electrochemical characterization of Nİ Tİ Nb shape memory alloy in artificial saliva,Materials and Corrosion(2012), 63(9),807-812
4. Zeng Z.Y., Hu C.E., Cai L.C., Chen X.R.,. Jing F.Q, First Principles Determination of the Structure, Elastic Constant, Phase Diagram and Thermodynamics of NiTi Alloy, Pysica B, 405 (2010) 3665-3672
5. Carroll Wİ.M., Kelly M.J., Corrosion behavior of nitinol wires in body fluid environments, Biomed Mater Res 67A,(2003),1123-1130
6. Li P., Wu G., Xu R., Wang W., Wu S., Weng W.K.,Chu P.K., In vitro corrosion inhibition on biomedical shape memory by plasma-polymerized allykamine film, Materials letters (2012), 89, 51-54
7. Hansen A. W., Führ L.T., Antonini L.M., Villarinho D.J.,Marino C.E.B., Malfatti C.F., The electrochemical behavior of the NiTi alloy in different simulated body fluids, Materials research (2015) 18 (1), 184-190
8. Bahraminasab M. and Sahari B.B., NİTİ Shape Memory Alloys, Promising Materials in Orthopedic Applications,http://dx.doi.org/10.5772/52228
9. Es-souni M., Es-souni M., Brandies H.F., On the transformation behaviour, mechanical properties and biocompability of two NiTi based shape memory alloys:NiTi42 and NiTi42Cu7, Biometarials, (2001), 22, 2153-2161
10. Kok M., Pirge G., Aydogdu Y., Isothermal Oxidation Study on NiMnGa Ferromagnetic Shape Memory Alloy at 600-1000 °C, Applied Surface Science (2013), 268 ,136-140
11. Kok M., Yildiz K., Oxidation parameters determination of Cu-Al-Ni-Fe shape-memory alloy at high temperatures, Applied Physics A: Materials Science And Processing, 116 (4), 2045-2050,2014
12. http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1992/illpres/oxidation.html
13. Aboutalebi M.R., Karimzadeh M., Salehi M.T., Abbasi S.M., Morakabati M., Influences of aging and thermomechanical treatments on the martensitic transformation and superelasticity of highly Ni-rich Ti-51.5 at.% Ni shape memory alloy, Thermochimica Acta, 616 14–19,2015